

Review

Synthesis and Properties of SBA-15 Modified with Non-Noble Metals

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Abstract: Modification of SBA-15 with non-noble metal leads to functional materials, which can be applied as gas sensors, adsorbents, and catalysts of various reactions. The new materials contain up to four various metals, which are deposited consecutively or simultaneously at various concentrations ranging from a fraction of 1% to an amount that is comparable with the mass of silica-support. These materials contain metals at various oxidation levels, usually as oxides, which occur in crystalline form (a typical crystallite size of about 10 nm matches the width of the SBA-15 channels), but in a few other materials, crystalline metal compounds have not been detected. Many researchers have provided detailed physico-chemical characteristics of SBA-15 modified with non-noble metals by the means of various microscopic and spectroscopic techniques.

Keywords: BET; XRD; TEM; FTIR; TGA; Raman

1. Introduction

This present review is devoted exclusively to non-noble metal-SBA-15 composites. These materials inherit periodic structures, high specific surface areas, and high thermal stabilities (up to about 700 °C) after SBA-15, and they show a wide variety of chemical properties that are inherited after the metallic components. Composites noble metal-SBA-15 were extensively studied, especially in the context of their catalytic properties. The noble metals were deposited on silica-only SBA-15 [1] or on non-noble metal-SBA-15 composites [2,3], but materials containing noble metals are outside the scope of the present review. There are specific problems in non-noble metal-SBA-15 composites, which need different approaches to noble metal-SBA-15 composites. For example, noble metals occur in an elementary (metallic) form, while non-noble metals occur in various chemical forms, which differ in the degree of oxidation of the metal (including but not limited to elementary metal), the degree of hydration, etc. Moreover on top of metal, oxygen, and hydrogen, composites with non-noble metals may contain other elements. Particular studies reported in the literature differ in many aspects, including the type of metal(s), the fraction of metal(s), the reaction being catalyzed, the availability of physico-chemical data obtained by different methods, etc. It is practically impossible to extract the effect of one variable from such a set of literature data. Impregnation with metal precursors often leads to a mixture of bulk metal oxides and silica, rather than to a real composite material. This is a real challenge in the synthesis of metal-SBA-15 composites, and various methods (e.g., addition of complexing agents) were used to avoid this problem.

The catalytic properties of SBA-15-metal composites were discussed (among many other materials) in several reviews. The catalysts containing non-noble metals, and various porous silicas (including SBA-15) are often considered as one class of materials. For example, Singh et al. [4] reviewed catalysts for reforming techniques. They especially emphasized the porous network of SBA-15 support as a factor limiting the growth of crystals of supported metal compounds. Very often, the catalysts

containing noble and non-noble metals are considered as one class of materials [5]. Usman et al. [6] reviewed catalysts of the dry reforming of methane, and discussed Ni-SBA-15 composites, among many other catalysts (chiefly Ni, Rh, and Pt supported on various oxides), and their study makes it possible to assess the influence of the support (SBA-15) on the catalytic activity, and to compare different supports. Ziolk and Sobczak [7] reviewed Nb-modified ordered silicas (including SBA-15) as supports of Cu, Ag, Au, and Pt, provided their physico-chemical characterization (XRD, X-rays diffraction, UV, ultraviolet-vis spectroscopy, H₂-TPR, temperature-programmed desorption, FTIR, Fourier transform infrared spectroscopy, EPR, electron paramagnetic resonance), and discussed the role of the support in the catalytic activities of their catalysts (especially in oxidation of methanol). Debecker et al. [8] reviewed mesoporous mixed oxide catalysts, and they compared Ti-modified SBA-15 with several other catalysts. Akbari et al. [9] reviewed catalysts of oxidation reactions, and discussed Ni-, Cu-, Ga-, In-, W-, and Fe-SBA-15 composites among many other catalysts (metal oxides and composites thereof).

On top of catalysis, several other potential applications of non-noble metal-SBA-15 composites have been considered. Z1 = 2 et al. [10] summarized recent studies demonstrating the application of W-modified, Pd- and Sn-, Cr- and W-, and Ag- and Sn-modified SBA-15 (among other materials) as gas sensors (a broad range of target gases). Yang [11] applied Bi-modified SBA-15 as a material for the capture of iodine (especially of I-129) and its stable storage. A short section in this review is devoted to the adsorption properties of metal-modified SBA-15, but most of the presented results refer to their catalytic properties.

2. Materials and Methods

The chemical composition of the composites, preparation methods, and the chemical forms of the metals in the composites reported in the recent literature [12–68] are summarized in Table S1 (supplementary material). Each composite was given a unique code that is used in further discussions. The composites are ordered by their codes in the table. Our codes consist of the names of metallic elements and numbers, and they differ from the codes used for the same composites in previous publications. The list of the chemical elements used in the code does not fully describe the chemical composition of the composite, and only up to two elements are indicated in the codes, while certain composites in Table S1 contain three or even four metallic elements. An exhaustive list of metallic elements, in particular composites, is reported in the second column of Table S1. Most studies of SBA-15 metal composites report their quantitative compositions, but different authors express metal concentrations by different methods (mass ratio, molar ratio, etc.) In this study, we used a unified approach, and all concentrations were expressed in terms of Si-to-metal atomic (molar) ratios. The compositions reported in the original publications were re-calculated when necessary. These concentrations are reported in the third column of Table S1, and large numbers correspond to low metal concentrations. The preparation of the composites is briefly described in the fifth column. We only gave a short description: “one pot” for metals added in the course of synthesis of SBA-15, etc., and the metal precursor was specified. Long descriptions were avoided, and more details that can be found in the original literature cited in the last column are in the references therein. Empty cells denote that certain information was not applicable or not reported.

Most composites used as catalysts were obtained by the impregnation of the original SBA-15 with aqueous solutions of simple inorganic salts of certain metal(s), followed by calcination, and different metal concentrations in the composite were achieved by the adjustment of metal concentration in solution. A few composites were obtained by impregnation with solutions in non-aqueous solvents, or in the presence of complexing agents in solution. One-pot syntheses and CVD were far less popular than impregnation.

Composites based upon SBA-15 containing Ni (with or without other metals) were studied in recent publications more often than in composites containing other non-noble metals, followed by composites containing Co or Ce (with or without other metals), while composites without Ni, Co, or

Ce were less popular. There was an obvious correlation between the catalytic properties of pure oxides of Ni, Co, and Ce, and catalytic properties of composites containing these oxides. The Si:metal atomic ratio in most catalysts was in the range of 5–30 in monometallic catalysts. In the catalysts containing more than one metal, the second (less abundant) metallic component was often added at very low concentrations (Si:metal atomic ratio > 100). Metals occurred in the form of oxides at various degrees of oxidation in most composites. Metallic Ni (pure or as an alloy with another metal) was found in a few composites. Spinel-type or perovskite-type mixed oxides were reported in a few composites. The formation of crystalline silicates was only observed in a few metal-SBA-15 composites containing Mg.

The methods used for the characterization of the composites (ordered by their codes), and the results obtained by nitrogen adsorption at its boiling point, and by XRD, are summarized in Table S2. The original acronyms used by the authors of cited papers are reported in Table S2, and sometimes one method is given various acronyms. The explanation of the codes of composites (detailed composition) can be found in Table S1. Most studies of SBA-15-metal composites report their specific surface areas, which are presented in the third column of Table S2. The SSA, specific surface area of original SBA-15 is given in the second column when available and applicable (e.g., there is no “original SBA-15” for one-pot synthesis). All SSA are rounded to 1 m²/g. The SSA is crucial as the property defining the ability of the composite to adsorb gaseous compounds. The size of crystallites and structures from XRD are reported in the fourth column. Several publications report the size of crystals of the metal compound from TEM, transmission electron microscopy (together with or instead of the size from XRD), but the size from microscopy is not reported in Table S2. In a few materials, the sizes from XRD and from TEM match, but in a few other composites, they do not. The size of the crystals has been emphasized as the parameter defining the catalytic activity of the composite. The fifth column of Table S2 shows a great variety of techniques other than SSA, and XRD. Actually, most abbreviations used in this review and summarized in the abbreviation list refer to various analytical techniques. Only a limited number of techniques were used in particular studies, and this can be explained by the limited availability of expensive equipment. Table S2 is a good illustration of two contradictory approaches used in catalytic studies. Several scientists prefer to experimentally study the catalytic activity of a series of catalysts in the reaction of interest first, and then follow this with physico-chemical characterization of the most promising specimens. The opposite approach is to provide detailed physico-chemical characterization of all specimens first, and then select promising specimens based on that characterization.

Table S2 shows that three to five different techniques (including SSA and XRD) were used in most studies to characterize particular composites. It should be emphasized that the term SBA-15 refers to a broad class of materials having a SSA in the range of 600–900 m²/g, and they also differ in their small-angle XRD patterns. Most composites had lower SSAs than the original SSA-15, but their SSAs were still very high (several hundred m²/g). A few composites showed exceptional behaviors. In Ce1, Ce3, Ce5, Ce11, Ce12, Ce13, and Ce15, the SSA was substantially higher than that of the original silica. These materials contained Ce as the only metallic component at very different concentrations (Si:Ce atomic ratios from 8 to 1000). In contrast La/Ni1, La/Ni2, and La/Ni3, had specific surface areas below 100 m²/g, that is, lower by an order of magnitude than the original silica. The sizes of the crystallites reported in the fourth column are often about 10 nm, and they match the diameters of the channels in the hexagonal network of SBA-15. This result confirms that SBA-15 confines the size of the crystals to the width of its channels.

3. Results and Discussion

In spite of their high SSAs, very few studies demonstrated possible application of non-noble metal-SBA-15 composites as adsorbents. A few examples are presented in Table 1.

Apparently, the ability of Ni-SBA-15 to adsorb hydrogen was the only adsorption property of the non-noble metal-SBA-15 composites, which has attracted a substantial amount of attention of scientists

over the recent few years. This process was studied over a wide range of temperatures, ranging from the boiling point of nitrogen to the limit of thermal stability of SBA-15.

Table 1. SBA-15 and SBA-15-metal composites as adsorbents.

Metal/Code	Gas/Liquid, $t/^\circ\text{C}$, Equilibration Time	Adsorbate	Concentration Range	Result	Reference
Ni2	Gas, 750, 1 h	Hydrogen	3% H ₂ /Ar	0.023 mmol/g Ni2	[46]
Ni3				0.068 mmol/g Ni3	
Ni4				0.055 mmol/g Ni4	
Ni5	Gas, -195, 1 h	Hydrogen	112 kPa	76.8 mL/g Ni5	[47]
	Gas, 30, 1 h		4000 kPa	17.6 mL/g Ni6	

Several examples of catalytic activity of SBA-15-metal composites are presented in Table 2. A few authors studied the catalytic activity of the original SBA-15 (no metal added) as a reference. Silica-only SBA-15 are presented in the upper part of Table 2 with codes None (none is for no metal added). The other materials are ordered by their codes, as in the other tables. Different authors have used different research strategies:

- a series of catalysts used to study one reaction at the same conditions,
- one catalyst used to study one reaction at various conditions (temperature, time of equilibration),
- one catalyst used to study multiple reactions,

and combinations thereof. The results are also presented in different formats in the original publications. In Table 2, we limited ourselves to the presentation of a few selected details. The reaction is briefly described in the second column, and the temperature t is given in the third column. In the studies performed at various temperatures with the same catalysts, the results obtained at each temperature are presented as a separate entry in the table. In parallel reactions (the same substrates give different products), two different approaches appear in the literature. In several papers, the overall conversion % is reported, followed by the selectivities for particular products (which add up to 100%). In other publications, the conversion percentages to certain products are reported, which may but not necessarily add up to 100%. In Table 2, we used the convention used by the authors of particular original papers. In the studies with various equilibration times, the conversion percentage in the fourth column is followed by the equilibration time in parentheses.

A broad variety of chemical reactions have been studied, as shown in the second column of Table 2. Many studies were performed at high temperatures ($>700^\circ\text{C}$), which are higher than the limit of long-term thermal stability for SBA-15. Although the presence of metallic elements may improve the thermal stability of SBA-15, the degradation of the catalyst and the change of its chemical and physical properties in the course of the catalytic reactions performed at $>700^\circ\text{C}$ is very likely. Therefore, processes occurring at lower temperatures are more promising in the view of possible practical applications. Unfortunately, the temperature is critical for a substantial conversion rate in many reactions. For example, in the conversion of carbon dioxide to carbon oxide and hydrogen catalyzed by Zr/Ce₂, the increase in the temperature from 620 to 750 $^\circ\text{C}$ improved the conversion rate from 58% to 100%. The problem is that the later temperature rise leads to degradation of the catalyst. Thus, we have a difficult choice between a high conversion rate and a long catalyst lifetime. This problem occurs in many other examples presented in Table 2; e.g., with the conversion of methane to hydrogen as catalyzed by Ni63 and Ni64. We would also like to emphasize that the results of thermal analysis may be misleading in the assessment of long-term thermal stability. Many publications report the results of fast scans (10 K/min or more), which only reflect short-term stability, and they substantially overrate the long-term thermal stability. Fortunately many reactions, e.g., of syngas to methane catalyzed by Ni20–Ni22, show a 100% or an almost 100% conversion at temperatures as low as 400 $^\circ\text{C}$, when the SBA-15 support is stable against thermal degradation.

Table 2. SBA-15 and SBA-15-metal composites as catalysts.

Metal/Code	Reaction	t , °C	Conversion, % Equilibration Time	Selectivity %	Reference
None1	Degradation of quinoline	300	3		[16]
None2	Reaction of diphenyl carbonate with isosorbide to poly(isosorbide carbonate)	240	67		[18]
None3	Conversion of 2,5-hexanedione to 2,5-dimethylfuran	350	8	19	[26]
	Conversion of 2,5-hexanedione to 3-methyl-2-cyclopentenone			81	
None4	Conversion of acetic acid to hydrogen	750	74	2	[61]
Al3	Esterification of acetic acid with n-butanol	80	70		
Al3	Benzylation of anisole	100	12		
Al4	Esterification of acetic acid with n-butanol	80	80		
Al4	Benzylation of anisole	100	25		[12]
Al5	Esterification of acetic acid with n-butanol	80	73		
Al5	Benzylation of anisole	100	51		
Al6	Esterification of acetic acid with n-butanol	80	58		
Al6	Benzylation of anisole	100	55		
Al15	Decarboxylation of methyl palmitate to alkane	340	45	65	[14]
Al16			69	75	
Al17			78	72	
Al21	Degradation of quinoline	300	8		[16]
Ca2	Reaction of diphenyl carbonate with isosorbide to poly(isosorbide carbonate)	240	82		[18]
Ca3			88		
Ca4			94		
Ca5			95		
Ca6			94		
Ca7			90		
Ce6			Conversion of toluene to carbon dioxide	360	
	Conversion of ethyl acetate to ethanol	81	31		

Table 2. Cont.

Metal/Code	Reaction	t , °C	Conversion, % Equilibration Time	Selectivity %	Reference		
Ce15	Conversion of 2,5-hexanedione to 2,5-dimethylfuran	350	51	3	[26]		
	Conversion of 2,5-hexanedione to 3-methyl-2-cyclopentenone			97			
	Oxidation of methanol to methanal	250	7	21			
		350	13	50			
	Conversion of methanol to dimethyl ether	250	7	4			
		350	13	3			
	Conversion of methanol to methyl formate	250	7	5			
		350	13	40			
Ce/Ni8	Conversion of anisole to methoxycyclohexane	270	7	81	[25]		
		290	18	59			
Ce/Ni9		270	26	76			
		290	29	55			
Ce/Ni10		270	28	70			
		290	33	49			
Ce/Ni11		Conversion of methanol to hydrogen	650	97		85	[27]
Ce/Ni12				98		90	
Ce/Ni13	100			98			
Ce/Ni14	98			85			
Ce/Zr1	Conversion of 2,5-hexanedione to 2,5-dimethylfuran	350	46	15	[26]		
	Conversion of 2,5-hexanedione to 3-methyl-2-cyclopentenone			85			
	Oxidation of methanol to methanal	250	5	39			
	Conversion of methanol to methyl formate			13			
	Conversion of methanol to dimethyl ether			44			
	Oxidation of methanol to methanal			48			
	Conversion of methanol to methyl formate	350	17	36			
	Conversion of methanol to dimethyl ether			10			

Table 2. Cont.

Metal/Code	Reaction	t , °C	Conversion, % Equilibration Time	Selectivity %	Reference
Ce/Zr2	Oxidation of methanol to methanal	250	3	33 *	[26]
	Conversion of methanol to dimethyl ether			52 *	
	Conversion of methanol to methyl formate			25 *	
	Conversion of 2,5-hexanedione to 2,5-dimethylfuran	350	55	18	
	Conversion of 2,5-hexanedione to 3-methyl-2-cyclopentenone			82	
	Conversion of methanol to methyl formate			26	
	Oxidation of methanol to methanal			40	
	Conversion of methanol to dimethyl ether			30	
Co1	Conversion of benzene to CO ₂ and H ₂ O (oxidation of benzene)	240	48		[20]
		255	100		
Co5	Epoxidation of styrene with oxygen	100	70	63	[29]
			82	64	
			92	63	
			94	66	
			48	55	
Co14	Conversion of CO ₂ to CO	753	40		[32]
	Conversion of CH ₄ to H ₂	728	44		
Co15	Dry reforming of CH ₄ with CO ₂ (conversion CH ₄)	700	20		[33]
Co16	Conversion of CH ₄ to H ₂	550	22		[34]
		700	78		
		550	18		
Co17	Conversion of CO ₂ to CO	700	90		
		750	0		
Co18	Dry reforming of CH ₄ with CO ₂ (conversion of CH ₄)	550	2		[36]
		600	8		
		700	24		

Table 2. Cont.

Metal/Code	Reaction	t , °C	Conversion, % Equilibration Time	Selectivity %	Reference
Co/Ce1	Conversion of benzene to CO ₂ and H ₂ O (oxidation of benzene)	280	51		[20]
		320	100		
Co/Ce2		220	10		
		260	50		
		275	90		
Co/Ce3		220	10		
		265	50		
		300	90		
Co/Ce4		245	10		
		280	50		
Co/Ce5	Oxidation of benzene	300	90		[22]
		245	10		
		300	50		
Co/Ce6		316	90		
		255	10		
		319	50		
Co/Ce7		340	90		
		270	10		
		340	50		
		372	90		

Table 2. Cont.

Metal/Code	Reaction	$t, ^\circ\text{C}$	Conversion, % Equilibration Time	Selectivity %	Reference
Co/Mo1	Hydrodesulfurization of dibenzothiophene	300	16 (4 h)		[37]
Co/Mo2			37 (8 h)		
Co/Mo3			25 (4 h)		
Co/Mo4			53 (8 h)		
Co/Mo5			30 (4 h)		
Co/Mo6			63 (8 h)		
Co/Mo7			34 (4 h)		
Co/Mo8			62 (8 h)		
Co/Mo9			38 (4 h)		
Co/Mo10			76 (8 h)		
Co/Mo11			48 (4 h)		
Co/Mo12			92 (8 h)		
Co/Mo13			22 (4 h)		
Co/Mo14			43 (8 h)		
Co/Mo15			30 (4 h)		
Co/Mo16			62 (8 h)		
Co/Mo17			35 (4 h)		
Co/Mo18			77 (8 h)		
Co/Ni1	Conversion of CH_4 to H_2	700	55		[38]
Co/Ni2	Conversion of CO_2 to CO		69		
Co/Ni3	Conversion of CH_4 to H_2		76		
Co/Ni4	Conversion of CO_2 to CO		81		
Co/Ni5	Conversion of CH_4 to H_2		45		
Co/Ni6	Conversion of CO_2 to CO		60		
Co/Ni7	Conversion of CO_2 to CO		80		
Co/Ni8	Conversion of CH_4 to H_2		74		

Table 2. Cont.

Metal/Code	Reaction	$t, ^\circ\text{C}$	Conversion, % Equilibration Time	Selectivity %	Reference	
Co/Ru1	Conversion of CH ₄ to H ₂	775	42		[32]	
	Conversion of CO ₂ to CO	750	40			
Co/Ru2	Conversion of CH ₄ to H ₂	790	82			
	Conversion of CO ₂ to CO		71			
Co/Ru3	Conversion of CO ₂ to CO	762	63			
	Conversion of CH ₄ to H ₂	790	69			
Cr1	Epoxidation of styrene with oxygen	100	13	48	[29]	
Cu1	Conversion of ethyl acetate to ethanol	360	17	22	[23]	
	Conversion of toluene to carbon dioxide		58	90		
Cu2	Reduction of NO to N ₂	440	30		[39]	
		510	45			
Cu3		440	40			
		490	55			
Cu4		440	7			
		490	20			
Cu5	Epoxidation of styrene with oxygen	100	0	0	[29]	
Cu/Al1	Decarboxylation of methyl palmitate to alkane	340	75	72	[14]	
Cu/Ce1	Conversion of toluene to carbon dioxide	360	65	93	[23]	
	Conversion of ethyl acetate to ethanol		50	10		
Cu/Ce2	Conversion of toluene to carbon dioxide		71	91		
	Conversion of ethyl acetate to ethanol		60	13		
Cu/Ce3	Conversion of toluene to carbon dioxide		76	94		
	Conversion of ethyl acetate to ethanol		91	7		

Table 2. Cont.

Metal/Code	Reaction	$t, ^\circ\text{C}$	Conversion, % Equilibration Time	Selectivity %	Reference	
Cu/Ce4	Conversion of methanol to methyl formate	250	6	85	[26]	
Cu/Ce4	Oxidation of methanol to methanal			6		
Cu/Ce4	Conversion of methanol to dimethyl ether			0		
Cu/Ce5	Conversion of methanol to dimethyl ether			2		
	Conversion of methanol to methyl formate			87		
	Oxidation of methanol to methanal			9		
Cu/Ce6	Conversion of methanol to methyl formate			74		
	Conversion of methanol to dimethyl ether			1		
	Oxidation of methanol to methanal			18		
Cu/Ni1	Conversion of cinnamaldehyde to hydrocinnamyl alcohol			130		60
	Oxidation of carbon oxide to carbon dioxide	160	27			
Cu/Ni2	Conversion of cinnamaldehyde to hydrocinnamyl alcohol	130	60	10		
	Oxidation of carbon oxide to carbon dioxide	160	40			
Cu/Ni3	Conversion of cinnamaldehyde to hydrocinnamyl alcohol	130	60	24		
	Oxidation of carbon oxide to carbon dioxide	160	43			
Cu/Ni4	Conversion of cinnamaldehyde to hydrocinnamyl alcohol	130	60	20		
	Oxidation of carbon oxide to carbon dioxide	160	50			
Cu/Zn1	Decarboxylation of methyl palmitate to alkane	340	71	78	[14]	
Cu/Zr1	Oxidation of methanol to methanal	250	15	16	[26]	
	Conversion of methanol to methyl formate			68		
	Conversion of methanol to dimethyl ether			5		
Fe5	Epoxidation of styrene with oxygen	100	21	56	[29]	
Ga1	Degradation of quinoline	300	5		[16]	

Table 2. Cont.

Metal/Code	Reaction	t , °C	Conversion, % Equilibration Time	Selectivity %	Reference
K/Mo2	Conversion of CO, H ₂ S, H ₂ to methanethiol	275	61	40	[42]
		300	62	47	
		325	63	45	
		350	64	38	
		375	64	26	
La/Ni1	Dry reforming of CH ₄ with CO ₂ (conversion of CH ₄)	600	63	[43]	
La/Ni2		700	88		
La/Ni3		600	69		
		700	82		
La/Ni4		Conversion of CH ₄ to H ₂	600		42
	750		95	97	
	Conversion of CO ₂ to CO	600	40	[44]	
		750	80		
Mn1	Epoxidation of styrene with oxygen	100	3	36	[29]
Ni1	Conversion of methane to hydrogen	750	88	[45]	
	Conversion of carbon dioxide to carbon oxide		86		
Ni2	Conversion of methane to hydrogen	500	20	[46]	
		700	70		
	Conversion of carbon dioxide to carbon oxide	500	25		
		600	65		
		700	75		
Ni3	Conversion of methane to hydrogen	500	15	[46]	
		700	75		
	Conversion of carbon dioxide to carbon oxide and hydrogen	500	20		
		600	50		

Table 2. Cont.

Metal/Code	Reaction	t_r , °C	Conversion, % Equilibration Time	Selectivity %	Reference
Ni4	Conversion of carbon dioxide to carbon oxide and hydrogen	500	30		[46]
		600	100		
	Conversion of methane to hydrogen	500	18		
		700	80		
Ni6	Epoxidation of styrene with oxygen	100	6	38	[29]
Ni7	Methane reforming with CO ₂ for hydrogen and syngas production (conversion of methane)	600	49		[24]
		750	79		
Ni8	Conversion of CH ₄ to H ₂	550	10		[48]
		700	55		
	Conversion of CO ₂ to CO	550	20		
		700	77		
Ni9	Conversion of glycerol to H ₂	600	90	53	[17]
Ni14	Conversion CH ₄ to CO ₂ and CO (selectivity for CO ₂)	400	5	97	[49]
		450	15	91	
		500	20	87	
		550	25	83	
Ni15	Conversion of CH ₄ to H ₂		7		[50]
	Conversion of CO ₂ to CO		7		
Ni16	Conversion of CH ₄ to H ₂	650	62		[50]
	Conversion of CO ₂ to CO		70		
Ni17	Conversion of CH ₄ to H ₂		20		[50]
	Conversion of CO ₂ to CO		27		
Ni18	Conversion of CH ₄ to H ₂	550	8		[51]
		650	35		
	Conversion of CO ₂ to CO	550	16		
		650	47		
Ni19	Dry reforming of CH ₄ with CO ₂ (conversion CH ₄)	700	77		[33]

Table 2. Cont.

Metal/Code	Reaction	t_r , °C	Conversion, % Equilibration Time	Selectivity %	Reference			
Ni20	Reaction of syngas to methane (conversion of CO)	400	83					
Ni21			100					
Ni22		250	64					
		400	98					
Ni23		250	40					
	400	100						
Ni24	Conversion of anisole to methoxycyclohexane	270	6	80	[25]			
		290	15	61				
Ni25	Reforming of propylene glycol (selectivity for H ₂)	630	88	57	[53]			
Ni29	Conversion of CH ₄ to H ₂	750	51					
	Conversion of CO ₂ to CO		65					
Ni30	Conversion of CO ₂ to CO		67					
	Conversion of CH ₄ to H ₂		56					
Ni31	Conversion of CO ₂ to CO		91					
	Conversion of CH ₄ to H ₂		76					
Ni32	Conversion of CO ₂ to CO		90					
	Conversion of CH ₄ to H ₂		77					
Ni33	Conversion of CH ₄ to H ₂		78					
	Conversion of CO ₂ to CO		92					
Ni34	Conversion of CH ₄ to H ₂		68					
	Conversion of CO ₂ to CO		78					
Ni35	Conversion of CH ₄ to H ₂		700			87		
	Conversion of CO ₂ to CO					94		
Ni36	Conversion of CH ₄ to H ₂		69		[55]			
	Conversion of CO ₂ to CO		79					

Table 2. Cont.

Metal/Code	Reaction	t , °C	Conversion, % Equilibration Time	Selectivity %	Reference
Ni37	Conversion of CH ₄ to H ₂	600	41		[56]
		800	93		
	Conversion of CO ₂ to CO	600	58		
		800	95		
Ni38	Conversion of CH ₄ to H ₂	600	40		
		800	92		
	Conversion of CO ₂ to CO	600	56		
		800	94		
Ni39	Conversion of CH ₄ to H ₂	600	41		
		800	93		
	Conversion of CO ₂ to CO	600	60		
		800	95		
Ni40	Conversion of CH ₄ to H ₂	600	40		
		800	93		
	Conversion of CO ₂ to CO	600	45		
		800	94		
Ni41	Conversion of naphthalene to tetralin		91		
	Conversion of naphthalene to <i>cis</i> -decalin		5		
Ni42	Conversion of naphthalene to tetralin		88		
	Conversion of naphthalene to <i>cis</i> -decalin		6		
Ni43	Conversion of naphthalene to tetralin		87		
	Conversion of naphthalene to <i>cis</i> -decalin		7		
Ni44	Conversion of naphthalene to tetralin	300	87		
	Conversion of naphthalene to <i>cis</i> -decalin		7		
Ni45	Conversion of naphthalene to tetralin		49		
	Conversion of naphthalene to <i>cis</i> -decalin		25		

[57]

Table 2. Cont.

Metal/Code	Reaction	$t, ^\circ\text{C}$	Conversion, % Equilibration Time	Selectivity %	Reference
Ni46	Conversion of naphthalene to tetralin		30		
	Conversion of naphthalene to <i>cis</i> -decalin		34		
Ni47	Conversion of naphthalene to tetralin		38		
	Conversion of naphthalene to <i>cis</i> -decalin		31		
Ni48	Conversion of naphthalene to tetralin		23		
	Conversion of naphthalene to <i>cis</i> -decalin		38		
Ni49	Conversion of naphthalene to tetralin		22		[57]
	Conversion of naphthalene to <i>cis</i> -decalin		40		
Ni50	Conversion of naphthalene to tetralin		12		
	Conversion of naphthalene to <i>cis</i> -decalin		44		
Ni51	Conversion of CH ₄ to H ₂		51		
	Conversion of CO ₂ to CO		65		
Ni52	Conversion of CH ₄ to H ₂		65		
	Conversion of CO ₂ to CO		75		
Ni53	Conversion of CH ₄ to H ₂	750	70		[58]
	Conversion of CO ₂ to CO		84		
Ni54	Conversion of CH ₄ to H ₂		79		
	Conversion of CO ₂ to CO		85		
Ni55	Conversion of CH ₄ to H ₂		76		
	Conversion of CO ₂ to CO		84		
Ni56	Conversion of CH ₄ to H ₂		60		
	Conversion of CO ₂ to CO		70		

Table 2. Cont.

Metal/Code	Reaction	$t, ^\circ\text{C}$	Conversion, % Equilibration Time	Selectivity %	Reference
Ni57	Conversion of ethanol to CO, CH ₄ , CO ₂	400	99	23 CH ₄ 12 CO ₂	[59]
Ni58			100	23 CH ₄ 12 CO ₂	
Ni59			100	24 CH ₄ 1 CO ₂	
Ni60			100	22 CH ₄ 1 CO ₂	
Ni61			100	24 CH ₄ 2 CO ₂	
Ni62	Conversion of methanol to hydrogen	650	85	62	[27]
Ni63	Conversion of methane to hydrogen	650	61		[60]
		800	94		
Ni64		650	62		
		800	96		
Ni65	Dry reforming of CH ₄ with CO ₂ (conversion CH ₄)	750	60		[35]
Ni66	Conversion of acetic acid to hydrogen	750	100	70	[61]
Ni67	Dry reforming of CH ₄ with CO ₂ (conversion of CH ₄)	550	9		[36]
Ni67		600	21		
Ni67		700	51		
Ni/Ca1	Conversion of glycerol to H ₂	600	98	53	[17]
Ni/Ce1	Methane reforming with CO ₂ for hydrogen and syngas production (conversion of methane)	600	52		[24]
		750	78		
Ni/Ce2		600	56		
		750	79		
Ni/Ce3		600	57		
	750	90			

Table 2. Cont.

Metal/Code	Reaction	t , °C	Conversion, % Equilibration Time	Selectivity %	Reference
Ni/Ce5	Conversion of CH ₄ to H ₂	400	6		[62]
		700	70		
	Conversion of CO ₂ to CO	400	5		
		700	66		
Ni/Ce6	Conversion of CH ₄ to H ₂	400	40		
		700	92		
	Conversion of CO ₂ to CO	400	42		
		700	85		
Ni/Ce7	Conversion of anisole to methoxycyclohexane	270	7	81	[25]
		290	15	61	
Ni/Ce8	Reforming of propylene glycol (selectivity for H ₂)	630	95	41	[53]
Ni/Ce10			96	38	
Ni/Ce11	Conversion of CH ₄ to H ₂	800	80		
	Conversion of CO ₂ to CO		80		
Ni/Ce12	Conversion of CH ₄ to H ₂	800	95		[63]
	Conversion of CO ₂ to CO		90		
Ni/Ce13	Conversion of CH ₄ to H ₂	800	90		
	Conversion of CO ₂ to CO		85		
Ni/Co1	Dry reforming of CH ₄ with CO ₂ (conversion of CH ₄)	700		75	[33]
Ni/Co2				73	
Ni/Co3				74	
Ni/Co4				50	
Ni/Co5				40	
Ni/Co7	Dry reforming of CH ₄ with CO ₂ (conversion CH ₄)	750	3		[35]

Table 2. Cont.

Metal/Code	Reaction	t_r , °C	Conversion, % Equilibration Time	Selectivity %	Reference
Ni/Mg1	Dry reforming of CH ₄ with CO ₂ (conversion of CH ₄)	800	85		[64]
Ni/Mg2			75		
Ni/Mg3			400		
Ni/Mg4			98		
Ni/Mg5			80		
Ni/Mg6	Conversion of glycerol to H ₂	600	99	53	[17]
Ni/Sm1	Conversion of CO ₂ to CO	550	14		[51]
		650	37		
	Conversion of CH ₄ to H ₂	550	8		
		650	21		
Ni/Sm2	Conversion of CO ₂ to CO	550	25		[51]
		650	56		
	Conversion of CH ₄ to H ₂	550	16		
		650	44		
Ni/Sm3	Conversion of CO ₂ to CO	550	33		[51]
		650	57		
	Conversion of CH ₄ to H ₂	550	25		
		650	54		
Ni/W4	Conversion of acetic acid to hydrogen	650	91	28	[61]
		700	93	24	
		750	93	45	
Ni/Y1	Conversion of CH ₄ to H ₂	550	13		[48]
		700	70		
	Conversion of CO ₂ to CO	550	22		
		700	55		
Ni/Zr1	Conversion of CH ₄ to H ₂	550	15		[48]
		700	45		
	Conversion of CO ₂ to CO	550	22		
		700	74		

Table 2. Cont.

Metal/Code	Reaction	t , °C	Conversion, % Equilibration Time	Selectivity %	Reference
Ni/Zr2	Reforming of propylene glycol (selectivity for H ₂)	630	97	36	[53]
Ni/Zr3	Conversion of acetic acid to hydrogen	750	100	58	[61]
Sm	Dry reforming of CH ₄ with CO ₂ (conversion of CH ₄)	550	2		[36]
		600	3		
		700	11		
Sm/Ni4	Conversion of CO ₂ to CO	550	35		[48]
		700	74		
	Conversion of CH ₄ to H ₂	550	28		
		700	72		
Sm/Ni2	Dry reforming of CH ₄ with CO ₂ (conversion of CH ₄)	550	19		[36]
		600	29		
		700	58		
V1	Oxidative dehydrogenation of propane to lower hydrocarbons, CO ₂ , CO		59		[65]
	Oxidative dehydrogenation of n-butane to lower hydrocarbons, CO ₂ , CO	540	63		
V2	Oxidative dehydrogenation of propane to lower hydrocarbons, CO ₂ , CO		62		
	Oxidative dehydrogenation of n-butane to lower hydrocarbons, CO ₂ , CO		95		
V3	Conversion of propane to propene	450	1	87	[66]
		500	3	80	
		550	12	68	
		600	16	66	
V4	Conversion of propane to propene	450	1	84	
		500	4	74	
		550	13	64	
		600	18	62	

Table 2. Cont.

Metal/Code	Reaction	$t, ^\circ\text{C}$	Conversion, % Equilibration Time	Selectivity %	Reference
V5		450	1	83	
		500	5	72	
		550	14	59	
		600	19	57	
V6	Conversion of propane to propene	450	1	73	[66]
		500	6	65	
		550	15	44	
		600	20	41	
V7		450	2	71	
		500	7	58	
		550	16	39	
		600	22	38	
Zn1	Epoxidation of styrene with oxygen	100	4	57	[29]
Zn/Al1	Decarboxylation of methyl palmitate to alkane	340	67	80	[14]
Zr2	Conversion of 2,5-hexanedione to 2,5-dimethylfuran	350	64	22	[26]
	Conversion of 2,5-hexanedione to 3-methyl-2-cyclopentenone		64	78	
	Conversion of methanol to dimethyl ether	250	1	100	
	Conversion of methanol to methyl formate			0	
	Oxidation of methanol to methanal			0	
	Conversion of methanol to dimethyl ether	350	19	43	
	Conversion of methanol to methyl formate			42	
Oxidation of methanol to methanal	28				
Zr3	Conversion of acetic acid to hydrogen	750	96	2	[61]

Table 2. Cont.

Metal/Code	Reaction	t , °C	Conversion, % Equilibration Time	Selectivity %	Reference
Zr/Ce1	Conversion of methane to hydrogen	740	91		[68]
		800	100		
	Conversion of carbon dioxide to carbon oxide and hydrogen	620	80		
		650	100		
Zr/Ce2	Conversion of methane to hydrogen	740	85		
		860	95		
	Conversion of carbon dioxide to carbon oxide and hydrogen	620	58		
		750	100		
Zr/Ce3	Conversion of methane to hydrogen	740	87		
		800	98		
	Conversion of carbon dioxide to carbon oxide and hydrogen	620	50		
		810	100		

* Error in the original paper.

The studies of the effect of the preparation method on the catalytic activity are rare. Two catalysts containing the same amount of Ca, and with very similar specific surface areas, obtained by the one-pot route on the one hand, and by wet impregnation on the other were studied, and the former was superior as a catalyst of reaction of diphenyl carbonate with isosorbide to poly(isosorbide carbonate) at 240 °C [18]. Three series of catalysts containing the same amounts of Co and Mo obtained by wet impregnation with different solutions were studied, and the materials obtained by impregnation with solutions containing EDTA, ethylenediaminetetraacetic acid were superior as catalysts of reaction of hydrodesulfurization of dibenzothiophene at 300 °C, as compared with materials obtained by impregnation with solutions containing citrate or without complexing agents [37]. All catalysts studied in [37] had similar specific surface areas, and they contained β -CoMoO₄. Four catalysts containing similar amounts of Cu and Ni, obtained by wet impregnation on the one hand, and by precipitation with carbonate or with urea on the other, were studied as catalysts of conversion of cinnamaldehyde to hydrocinnamyl alcohol at 130 °C and of oxidation of carbon oxide to carbon dioxide at 160 °C [40]. The catalyst obtained by precipitation with urea was superior to other catalysts in the oxidation of carbon oxide, and the catalyst obtained by precipitation with carbonate was more selective than other catalysts in the conversion of cinnamaldehyde to hydrocinnamyl alcohol. Interestingly enough, the efficient catalysts obtained by precipitation had lower SSA than less-efficient catalysts obtained by impregnation [40]. Three catalysts containing similar amounts of Ni, obtained by different methods were studied as catalysts of conversion of carbon dioxide to carbon oxide and hydrogen at 500 and 600 °C, and of the conversion of methane to hydrogen at 500 and 700 °C [46]. The catalyst obtained in mixed suspension with urea and ascorbic acid was more efficient than other catalysts in both reactions. Again, the most efficient catalysts had lower SSA than the less efficient catalysts [46]. Four catalysts containing the same amount of Ni, obtained by wet impregnation in the presence and absence of different complexing agents were studied as catalysts of conversion of CH₄ to H₂ and of the conversion of CO₂ to CO, both reactions at 600 and 800 °C [56]. The catalyst were equally efficient at 800 °C, and the catalyst obtained in absence of complexing agents was less efficient than catalysts obtained in the presence of complexing agents at 600 °C, although the effect was not very significant. Five series of catalysts containing the same amounts of Ni obtained by wet impregnation in the presence and absence of EDTA were studied as catalysts of conversion of naphthalene to tetralin on the one hand, and to *cis*-decalin on the other, at 300 °C [57]. Tetralin was the main product with catalysts synthesized in absence of complexing agents, especially with materials with low Ni concentration, and *cis*-decalin was the main product, with catalysts synthesized in the presence of EDTA, especially with materials with high Ni concentration. The catalysts synthesized in the presence of EDTA had lower specific surface areas than their counterparts containing the same amount of Ni, but synthesized in absence of complexing agents. Three catalysts containing the same amounts of Ni and Ce, obtained by wet impregnation at different conditions (ultrasounds, reflux) were studied as catalysts of methane reforming with CO₂ for hydrogen and syngas production at 600 and 750 °C [24]. The catalyst obtained by reflux was superior to the other catalysts, although the effect was not very significant.

4. Conclusions

Non-noble metal-SBA-15 composites have been extensively studied as compared with their counterparts, based on other types of ordered mesoporous silicas (MCM-41, FSM-16, KIT-6, etc.). In spite of their high specific surface areas, their potential applications as adsorbents have attracted little attention. In contrast, their catalytic properties were demonstrated in many studies. Composites containing Ni (with or without other metals) are especially promising as catalysts of numerous redox reactions. Not much work was done on the effect of the preparation method on the catalytic properties. Very likely, catalysts having the same composition as the materials already examined, but prepared in different ways (e.g., by wet impregnation in the presence of complexing agents) may show superior catalytic activities to the results in reported in Table 2. Further studies in this direction are greatly desired.

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Abbreviations:

BET	Brunauer, Emmett, Teller (isotherm of adsorption)
CVD	chemical vapor deposition
DRIFT	diffuse reflectance infrared Fourier transform (spectroscopy)
DRM	double resonance modulation (in spectroscopy)
DTA	differential thermal analysis
DTG	differential thermogravimetry
EDS	energy dispersive X-ray spectroscopy
EDXS	energy dispersive X-ray spectroscopy
EELS	electron energy loss spectroscopy
FFT	fast Fourier transform
FTIR	Fourier transform infrared (spectroscopy)
HR	high resolution (TEM)
MAS	magic angle spinning (NMR)
NMR	nuclear magnetic resonance
SEM	scanning electron microscopy
SSA	specific surface area
TEM	transmission electron microscopy
TG	thermogravimetry
TGA	thermogravimetric analysis
TPH	temperature-programmed hydrogenation
TPD	temperature-programmed desorption
TPO	temperature-programmed oxidation
TPR	temperature-programmed reduction
UV	ultraviolet
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy
XRD	X-rays diffraction
XRF	X-ray fluorescence

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