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Influence of modifying additives on the catalytic activity and stability of $Au/Fe_2O_3–MO_x$ catalysts for the WGS reaction

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The activity and stability of $Au/Fe_2O_3–MO_x$ catalysts (M = Zr, Mg, Ca, Ni, La, Cu, Zn, Al, Ba, Cr, Co, Ce, Mo, Bi, Ti, Mn) in water-gas shift reaction were investigated extensively. The WGS activity and stability of Au/Fe_2O_3 is improved significantly upon addition of ZrO_2 and to a lesser extend MgO, CaO, NiO, La_2O_3, Cr_2O_3, CuO. In contrast, Bi, Ti and Mn oxides seriously decrease the catalytic activity while additions of Zn, Al, Ba, Co, Ce and Mo oxides do not influence evidently the catalytic activity and its stability. Based on the characterization using the methods of BET-surface area and pore structure XRF, XRD, and H_2–TPR for some of as-prepared and spent samples, it could be concluded that the catalytic activity of gold catalysts supported on composite oxide of $Fe_2O_3–MO_x$ depends not only on the dispersion of the gold particles but also on the reduction property of composite oxide supports, regardless of the fluctuation of gold loading and some change of specific surface area and pore structure due to introduction of the modifying metal oxides. The improvement of catalytic stability may be attributed to the comparative stabilization of high dispersion of gold particles and uneasily sintering of Fe_3O_4 crystallites during the catalytic operation. However, the chemical (electronic) effects exerted by the modifying addition of metal oxides on the catalytic performance of gold catalyst may not be ruled out.

KEY WORDS: water-gas shift; gold catalyst; metal oxides; iron oxide; modification; catalytic stability.

1. Introduction

In almost all ammonia plants worldwide, the water-gas shift reaction (WGSR) is widely applied to oxidize carbon monoxide, which may irreversibly deactivate the ammonia synthesis catalyst and to increase the production of hydrogen as well. The adjustment of the carbon monoxide to hydrogen ratio in the synthesis gas is also implemented by the reaction [1,2]. Recently, fuel cell power generation is undergoing rapid development both for stationary and transportation applications wherein the "old-fashioned" reaction (WGSR) is a key step for removing CO formed by on-board reforming reaction, though the remaining of CO being further converted through preferential oxidation (PROX) [3]. In addition, because exhaust gases contain permanently 10–12% water, CO can be converted to CO_2 through the WGS reaction and the hydrogen produced is a very effective reductant for NO_x removal, providing an effective way for the control of our environment pollution [4]. Although the commercial $Cu–Zn–Al_2O_3$ low-temperature WGS catalyst hold perfect catalytic temperature, its use in the above applications is highly unlikely because of its air sensitivity, narrow operating temperature window, and careful activation in H_2. Many investigations showed that gold highly dispersed on the appropriate support manifests a highly catalytic activity in the low temperature WGS reaction [5,12]. It is generally known that high catalytic activity of supported gold catalysts depends strongly on the preparation method [8,13,14], the synthesis parameters [15], pretreatments conditions [16,17] the choice of the supports [18,20], all affecting the dispersion of the gold particles and the state and the structure of the supports. Moreover, the catalytic activity of the gold-containing systems decreased gradually during the catalytic run, meaning insufficient stability [21,22]. Therefore, most of the interest in gold catalysis has geared to find more efficient and stable support for it. The effect of the addition of modifier is explored widely on the catalytic performance of gold-based catalyst for various important reactions [21,23]. However, there is relatively little work devoted on the catalytic stability of gold catalyst in WGS reaction [31,32]. Tabakova et al. attempted to prepare highly active and more stable gold catalyst in WGS reaction by modification of Fe_2O_3 support with ZnO and ZrO_2. They found that the catalysts activity and stability depends not only on the degree of crystallinity of support, but also on the dispersion of gold particles, while the desirable effect of increased activity

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and stability by the modification was not achieved [31]. Recently, Venugopal et al. studied the catalytic of the modified Au/Fe_2O_3 catalysts with second metal and found that the order of activity at 373 K to be: Ru > Ni > Blank > Sn > Pb > Mn ≥ Cu > Tl > Co > Ag, while Ru > Ni > Bi > Cu > Pb > Ag > Tl > Blank > Sn > Mn > Co at 513 K, and that surprisingly bismuth, lead and thallium would not act as poisons for gold in the reaction [32].

In the present paper, we have investigated the WGSR activity and stability over gold-based catalyst supported on composite oxide of Fe_2O_3–MO_x (M = Zr, Mg, Ca, Ni, La, Cu, Zn, Al, Ba, Cr, Co, Ce, Mo, Bi, Ti, Mn), aiming at obtaining highly active and stable gold catalyst for possible industrial applications. The measured catalytic performance is related to the various characterization results to further understand the essence of the catalytic performance of supported gold catalyst.

2. Experimental

2.1. Catalyst preparation

Conventional co-precipitation method was applied to prepare Au/Fe_2O_3–MO_x catalysts using K_2CO_3 as precipitating agent. The aqueous solution of 1.0 M K_2CO_3 was firstly added to ca. 20 ml water at 333 K under vigorous stirring, the resultant pH value being 8.0. Then the aqueous mixture of 0.2 M $HAuCl_4$, 1.0 M $Fe(NO_3)_3$ and 1.0 M $M(NO_3)_x$ (M = Mg, Ca, Ni, La, Cu, Zn, Al, Co, Ce, Mn), or $ZrOCl_2$,CrO_3, $(NH_4)_6Mo_7O_{24}$ aqueous solution, with the atomic ratio Au/M/Fe being 1/1.56/30, was dropped over 5 min into the above alkaline solution. The formed suspension was digested for 1 h under stirring. After cooling naturally to room temperature, the resultant precipitate was alternatively centrifuged and washed several times until no AgCl precipitate was noted on dropping $AgNO_3$ solution into the filtrate. Further the paste was dried at 393 K, then heated to 573 K in static air at a heating rate of 5 K/min; calcination at 573 K continued for 2 h. The Au/Fe_2O_3–MO_x (M = Ba, Bi, Ti) catalysts were similarly prepared according to the above procedure except that the powder of Ba, Bi, Ti oxides was added to the suspension co-precipitated from $HAuCl_4$, $Fe(NO_3)_3$, and K_2CO_3 and mixed under stirring and further dispersed ultrasonically.

2.2. Characterization methods

2.2.1. Surface area and porous structure determination

Determination of surface area and the texture of the samples were made by the BET method from nitrogen sorption isotherms measured at liquid nitrogen temperature, using 'OMNISORP100CX'device. Prior to analysis, the sample was degassed 393 K until the vacuum inside the sample tube was more than 1×10^{-5} MPa.

2.2.2. X-ray fluorescence analysis

The bulk composition was determined by X-ray fluorescence (XRF) analysis performed on 'PHILPS Magixpw2424 XRF' (Rh target, X-ray tube most power 2.4 kW). The gold content was defined half-qualitatively by gold weight percent normalized on the weight of Fe_2O_3. The conversion equation is expressed as follows: $W_{Au}/(wt\%) = [(Au \times 2M_{Fe})/(Fe \times M_{Fe_2O_3})] \times 100\%$ wherein Au and e refers to the obtained relative weight of Au and Fe from XRF analysis respectively while M_{Fe} and $M_{Fe_2O_3}$ to the molecular weight of iron and its oxide. The content of additive element is obtained similarly.

2.2.3. X-ray powder diffraction

XRD measurement was performed on a Nihon Rigaku D/max-3C X-ray powder diffractometer with Cu Kα radiation (30 mA, 40 kV) over a 2θ range of 5°–90°. The obtained patterns were used to determine the phases present in the catalysts.

2.2.4. Temperature-programmed reduction (TPR)

H_2-TPR of the catalysts in fine powder form were carried out in a 'Micromeritics Autochem2910' instrument. A fresh sample weighing ca. 0.10 g was inserted into a U-shaped reactor made from quartz tubing of 6 mm i.d. the reactor firstly purged with high purity helium at room temperature for 1 h. TPR traces of the studied samples were then pursued in a reductive flow of 30 ml/min 10Vol.%H_2 in helium, on raising the system temperature linearly from temperature to 973 K at a ramp rate of 10 K/min. The rate of hydrogen consumption was monitored by the TCD of the instrument. A cold trap filled with a mixture of isopropanol and liquid was mounted in the gas line upstream of the TCD to remove the water vapor.

2.3. Activity and stability measurements

The catalytic activity of the samples in the WGS reaction was measured by using 'CO-CMAT9001 (HD. CO. LTD, Peiking, China)' at atmospheric pressure. A stainless steel tube with an inner diameter of 9 mm was chosen as the reactor tube. The sample (0.46 g, ca. 0.5 cm^3, 20–40 mesh size) was placed on quartz granules (10–12 mesh size) at the lower part of the reactor. The upper part of the catalyst bed was packed with the same quartz granules. The furnace temperature was controlled through a programmed controller. Prior to measurement, the samples were reduced in 10Vol.%H_2 balanced in N_2 at 473 K (heating rate, 3 K/min) and kept at 473 K for 3 h. The reactant gas mixture was passed through a vaporizer (355 K) at a space velocity of 10,000 h^{-1} ml/g-cat, before being fed into the vertical reactor that contained 10Vol.%CO, the rest being nitrogen. The product gas is directed through a condenser and sent to an on-line gas chromatograph

(Shimadzu GC-8A), where the CO content is analyzed. The catalytic activity of samples at 473 K was recorded consecutively until reaching stable value. The activity was expressed by the degree of conversion of CO, which is defined as follows: X (CO)% = $(1 - V'_{CO}/V_{CO}) \times 100\%$ $/(1 + V'_{CO})$ where V_{CO} and V'_{CO} is the inlet and outlet content of CO, respectively. The catalytic stability was defined as the on-line time (Δt, h) before the activity attaining stable value.

3. Results

3.1. Catalytic activity and stability

The catalytic activity of the studied samples along with the on-line (Δt, h) is shown exemplarily in figure 1 for the sake of clarity. It is clearly seen that the catalytic behavior of Au/Fe_2O_3 catalysts modified with different metal oxide vary remarkably. The initial catalytic activity (C_o, %) of the modified Au/Fe_2O_3 catalysts remains unchanged nearly upon adding of the metal oxide, except that the addition of Cr, Ce, Mo, Ti oxides results in decrease to some extent and Bi_2O_3, especially MnO_x seriously. Surprisingly, the Au/Fe_2O_3 catalyst modified by ZrO_2 shows the highest catalytic activity and stability, namely CO conversion close to the theoretical equilibrium value (99.9%) under our experimental conditions even after being on run for 58 h, whereas the sample modified with TiO_2 markedly decays with on-line time. The corresponding CO conversion decreases to be only 10% within 55 h. Although the activity of some catalysts becomes stable within shorter on-line time, the decrease value (ΔC) and the steady (C_s, %) of their activity both vary remarkably. The greater decrease of activity also means more poor stability, while the final steady activity is much important for practical application.

Therefore, only employing the on-line time before activity reaches steady activity value to characterize the catalytic stability for the investigated catalysts seems unreasonable. So here we employ a stability parameter (S, h^{-1}) defined as follows: $S = C_s/\Delta t \times \Delta C$ and the greater S value implies well stability, vice versa. The redefined stability parameters of the studied catalysts are listed in table 1, the initial, steady value (C_o, C_s, %) of their activity and the corresponding catalytic decrease value (ΔC), also included.

As seen from table 1, the modifying additives can be classified as the following three groups according to the steady activity combined with its stability. Addition of the first group metal oxides, especially ZrO_2, MgO, CaO, NiO, La_2O_3, CuO, CrO_3, ZnO, Al_2O_3 and BaO not only enhances the steady activity but also improve the catalytic stability of gold catalyst supported on composite oxide in low-temperature WGS reaction. Nevertheless the promotional effect becomes gradually less evident along with the above order. The catalytic activity and stability is almost unaffected by addition of the second group including CeO_2 and Co_2O_3. The additions of Mo_2O_3, Bi_2O_3, TiO_2, and MnO_x seriously decrease the catalytic performance of Au/Fe_2O_3 catalysts.

3.2. Catalyst characterization

3.2.1. BET surface area and porous structure

Change in surface area and porous structure of unmodified and modified Au/Fe_2O_3 catalysts before and after the title reaction are presented in tables 2, 3 and illustrated exemplarily in figures 2, 3, respectively.

From table 2, it can be seen that the additions of ZnO, Al_2O_3 increase the surface area of the fresh gold catalysts supported on the modified iron oxide, conversely doping the solid with Cu, Cr, Ba, Mo, Bi, Ti and

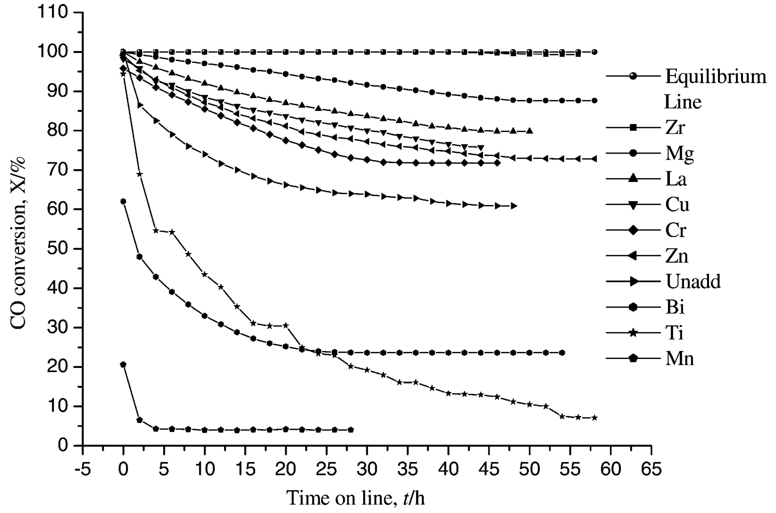

Figure 1. WGSR activity and stability of Au/Fe_2O_3 catalysts modified by various oxides Reaction temperature, 473 K; Vapor gas ratio, 1:1; space velocity, 10,000 h^{-1}.

Table 1
The catalytic activity and stability of Au/Fe_2O_3–MO_x catalysts in WGS reaction at 473 K

M	Zr	Mg	Ca	Ni	La	Cu	Cr	Zn	Al	Ba	Ce	Un	Co	Mo	Bi	Ti	Mn
C_0/(%)	99.2	99.2	99.2	99.2	99.2	98.2	95.8	99.1	99.2	98.2	93.0	99.2	99.2	94.2	62.0	94.4	20.6
Cs/(%)	99.2	87.6	83.7	80.5	80.0	76.0	71.8	73.1	71.0	69	62.2	61.0	59.2	50.4	23.7	7.2	4.0
Δt/(h)	0	48	36	48	44	42	34	48	52	50	38	44	52	48	28	54	4
ΔC/(%)	0	12.4	16.3	19.5	20.0	22.2	24.0	26.0	29.0	29.2	30.8	39.0	40.8	43.8	38.3	87.2	16.6
S/(h^{-1})	∞	0.15	0.14	0.09	0.09	0.08	0.09	0.06	0.05	0.05	0.05	0.04	0.03	0.02	0.02	0	0.06

Table 2
Surface area and porous data of the modified Au/Fe_2O_3–MO_x catalysts as prepared

M	Zr	Mg	Ca	Ni	La	Cu	Cr	Zn	Al	Ba	Ce	Un	Co	Mo	Bi	Ti	Mn
Sg/($m^2 \cdot g^{-1}$)	184	189	187	188	181	167	158	194	190	167	185	186	184	176	156	174	163
Rav/(nm)	3.78	3.44	n.m.	3.73	4.20	n.m.	5.03	n.m.	3.97	n.m.	4.46	3.33	n.m.	n.m.	4.87	4.38	3.62
Vp/($ml \cdot g^{-1}$)	0.35	0.33	n.m.	0.35	0.38	n.m.	0.40	n.m.	0.38	n.m.	0.41	0.31	n.m.	n.m.	0.38	0.38	0.30

Sg: Surface area; Rav: mean radius of pores; Vp: pore volume; n.m.: not measured.

Mn oxides apparently decrease its surface area, while the introductions of the rest oxides, i.e. Zr, Mg, Ca, Ni, La, Ce and Co oxides, only have a slight affect. In addition, some increase in the mean pore radius and pore volume is observed for gold catalysts modified with the metal oxides except for MnO_x. Neither the pore size distribution nor the pore structure of Au/Fe_2O_3–MO_x catalysts change significantly arising from the addition of metal oxide, most ranging 1.3–2.5 nm with optimal value ca. 1.70 nm, which is suggested by the exemplary curves shown in figures 2 (a) and 3 (a).

After catalytic operation, the surface area and pore volume of the investigated samples all greatly decreased as a result of sintering, accompanied with the enlargement of pore radius and widening of pore size distribution, as illustrated in table 3 and figure 2 (b). However, the pore structure of the spent catalysts all do not change markedly, revealed by the nitrogen sorption isotherms which are shown by exemplary curves in figure 3 (b).

3.2.2. XRF results

Table 4 shows the results of the content analysis of gold, iron, additive metal and potassium. Table 5 reports exemplarily the corresponding values for the spent samples.

Table 3
Surface area and porous data of the modified Au/Fe_2O_3–MO_x catalysts after WGS reaction

M	Zr	Mg	Ca	Un	Ti	Mn
Sg/($m^2 \cdot g^{-1}$)	49.1	39.3	65.4	4.01	35.0	40.0
Rav/(nm)	7.35	8.19	9.34	7.18	8.17	7.11
Vp/($ml \cdot g^{-1}$)	0.18	0.18	0.18	0.14	0.14	0.14

Note: See Table 2 for the denotation of the symbols.

It is found that no Cl^- is detected in the investigated samples while K^+ in occasional cases. It is also seen that the gold content of the modified gold catalysts are higher than that of the unmodified, especially MgO, CeO_2, MnO_x-doped samples wherein the gold content is even higher than the designed value, 8wt%, possibly implying the loss of iron oxide is much more serious than that of gold during the catalyst preparation. Thus it is concluded that the introduction of metal oxide will generally favor gold co-precipitation and/or reduce the gold loss during the washing step. Similarly, the content of additive oxide itself is affected to some extent depending strongly on its type. ZrO_2, MgO, CrO_3, ZnO, Al_2O_3 and Mo_2O_3 is not effectively introduced into the Au-containing iron oxide system through co-precipitation method, which will result in its serious loss in the course of the catalyst preparation. The content of the CaO and Co_2O_3 additives is almost comparable to the desired value. The higher content of the NiO, La_2O_3 CuO, CeO_2 and MnO_x than the corresponding desired value is also due to the assumption that the loss of iron oxide is much more serious than that of the additives during the preparation of the catalysts. For the case of introducing as metal powder form, most of BaO lost during the washing step whereas to less extent Bi_2O_3 and TiO_2. On the basis of comparison between the results of the fresh and spent samples (see tables 4, 5), it is found that after catalytic operation, the content of gold reduced apparently whereas that of the modifying elements did not change nearly.

3.2.3. XRD analysis

Figure 4 reports the XRD patterns of the Au/Fe_2O_3–MO_x and the unmodified catalysts before WGS reaction. It is clear that addition of MO_x to Au/Fe_2O_3 have

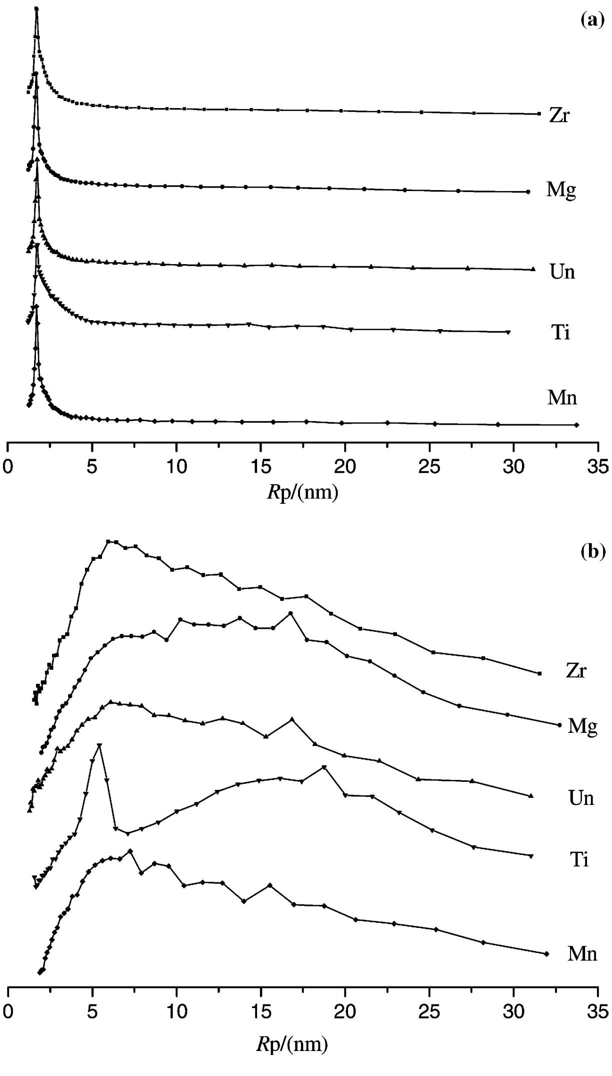

Figure 2. (a) Pore size distribution of Au/Fe_2O_3–MO_x catalysts as prepared. (b) Pore size distribution of Au/Fe_2O_3–MO_x catalysts after WGS reaction.

an evident effect on the dispersion of the Au particles and on the crystallization of the iron oxide support in the course of calcinations at 573 K. The two effects were found to depend strongly on the identity of the added MO_x, respectively. Addition of MO_x (M = Mg, Ca, Ni, La, Zn, Al, Ti) to Au/Fe_2O_3 seemed to stabilize the initially small Au particles and do not significantly affect the crystallization of iron oxide support. For the MnO_x, CeO_2, Co_2O_3, MoO_3 containing catalysts, small Au particles initially present on the unmodified catalyst sintered considerably during the calcination procedure, whereas addition of ZrO_2 improved the dispersion of Au particles to some extent. As for the change of the crystalline behavior of iron oxide support, added Cr_2O_3, Bi_2O_3 would separate as another Cr_2O_3 and unknown phase, respectively and iron oxide became crystallized evidently. Next, additions of BaO, CuO, MnO_x, MoO_3, TiO_2 slightly increased the degree of crystallinity of the iron oxide support.

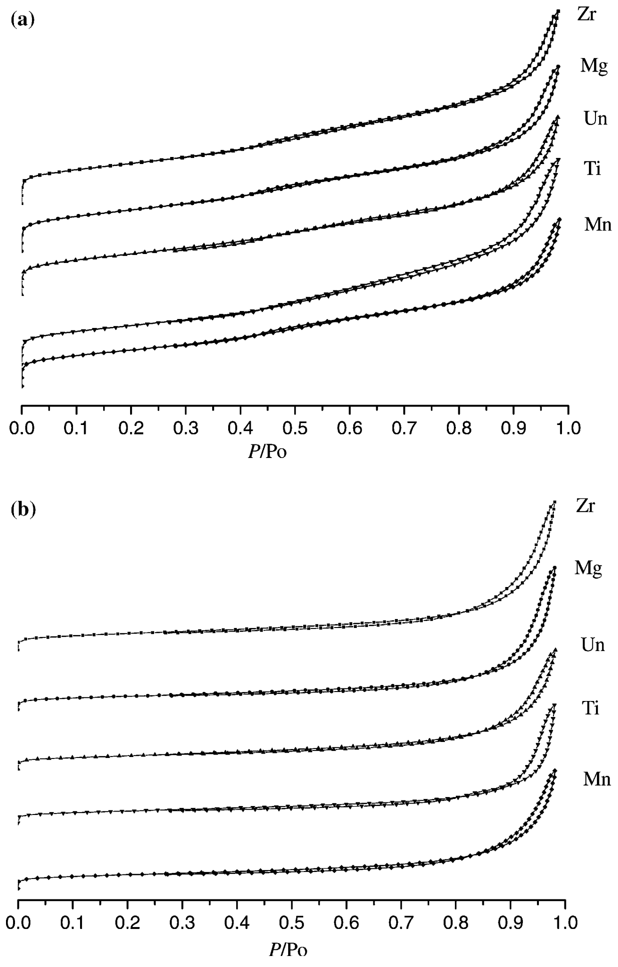

Figure 3. (a) Adsorption-desorption isotherms of Au/Fe_2O_3–MO_x catalysts as prepared. (b) Adsorption-desorption isotherms of Au/Fe_2O_3–MO_x catalysts after WGS reaction.

As seen from figure 5, the iron oxides all were reduced to magnetite phases during the catalytic run. The further sintering of Au particles also was observed, depending strongly on the kind of the added MO_x. Additions of ZrO_2 and TiO_2 obviously inhibited the growth of Au particle during catalytic operation, whereas addition of MnO_x accelerated markedly Au particles agglomeration. Next to $ZrO_2$and TiO_2, additions of MgO and CaO, to a lesser extent, suppressed the growth of Au particle. Similarly, the crystallite size of the magnetite was also dependent on the type of the added MO_x For the TiO_2, and MnO_x-modified catalysts, the intensity of Fe_3O_4 pattern peaks became stronger compared to that of the unmodified while conversely the additions of ZrO_2, MgO, and CaO.

3.2.4. H_2-TPR profiles

The TPR curves of the investigated Au/Fe_2O_3–MO_x catalysts are shown exemplarily in figure 6. The corresponding peak temperatures of all studied catalyst samples are listed in table 6. According to the

Table 4
XRF analysis for chemical compositions of Au/Fe_2O_3–MO_x catalysts as prepared

M	Zr	Mg	Ca	Ni	La	Cu	Cr	Zn	Al	Ba	Ce	Un	Co	Mo	Bi	Ti	Mn
W'_{Au}/(wt%)	6.76	8.13	7.28	7.65	7.31	6.27	7.58	7.00	7.82	6.70	9.78	6.11	7.25	7.88	7.19	7.42	9.69
W_M/(wt%)	6.01	1.60	2.64	3.87	9.16	4.19	4.09	4.31	1.78	9.05	9.23	0	3.89	6.32	13.78	3.16	3.62
W'_M/(wt%)	2.67	0.51	2.20	4.89	9.58	5.47	1.47	3.62	0.96	1.18	9.45	0	3.43	1.58	10.65	2.77	4.40
W'_K/(wt%)	0	0	0.07	0	0	0.24	0	0.08	0	0	0	0.87	0.16	0.19	0	0	0

literature data [33], the low temperature peaks (Tα1, 2) is ascribed to the transition $Fe_2O_3 \rightarrow Fe_3O_4$, whereas the other peak (Tβ) is attributed to the $Fe_3O_4 \rightarrow FeO$. Although it is observed widely that the presence of gold tends to catalyze the reduction of some of the iron present in the ferric oxide support, the reducibility of the Au-containing systems is strongly related to the preparation method and conditions, which is similar to the case of iron oxide alone [34]. Thus the pure iron oxide is also synthesized under the same conditions to be used as an exact reference. The pure α-Fe_2O_3 showed two distinct reduction signals, one at 640 K with a shoulder at 553 K and a high-temperature peak at 912 K. After introduction of gold through co-precipitation, the low-temperature peak is shifted markedly toward lower-temperature region whereas the other peak with a variation of ca. 20 K. As seen from table 6, it is evident that not only the reduction in the low temperature region but also the high temperature reduction of the Au-containing iron oxide is affected further remarkably due to the addition of the modifying metal oxide. Moreover, the samples' reduction behavior is dependent strongly on the identity of the modifier metal oxide. It was found that additions of Zr, Mg, Ca, Zn, Ti oxides shifted the Tα peaks to below 373 K. Next to these oxides, also additions of Ni, La, Al, Ce oxides and to a lesser extent Cu, Cr, Ba, Co, Bi oxides, were found to lower the Tα peak temperatures. However, additions of Mo_2O_3 and MnO_x would shift the Tβ peak to higher temperature. Although the Tβ speak is considered to be linked to the stability of the magnetite phase [2], the change of the reduction behavior of the studied catalysts in the high temperature region is not analyzed in details since we investigate the catalytic performance in the low temperature region.

Table 5
XRF analysis for chemical compositions of Au/Fe_2O_3–MO_x catalysts after WGS reaction

M	Zr	Mg	Ca	Un	Ti	Mn
W'_{Au}/(wt%)	6.29	6.93	7.40	5.84	6.63	8.96
W'_M/(wt%)	2.48	0.60	2.29	0	2.81	4.31
W'_K/(wt%)	0.22	0.06	0	0.65	0	0.55

4. Discussion

In the present work, we have explored extensively the promotion of various metal oxides on the WGS activity and stability at 473 K of Au/Fe_2O_3 catalysts prepared through co-precipitation method. It was found that the initial activity of the modified Au/Fe_2O_3 catalysts is not affected nearly due to addition of modifier metal oxide except that additions of Cr, Ce, Mo, Bi, Ti, Mn oxides will exert a detrimental effect. The steady catalytic activities over Au/Fe_2O_3–MO_x catalysts were found to obey the following order: $ZrO_2 > MgO > CaO > NiO \approx La_2O_3 > CuO > Cr_2O_3 \approx ZnO \approx Al_2O_3 \approx BaO > CeO_2 \approx$ Unadd $\approx CoO > MoO_3 > Bi_2O_3 > TiO_2 > MnOx$, (Unadd refers to the unmodified sample). Analysis of the data on surface area indicates that this parameter does not determine the catalytic activity of the modified Au/Fe_2O_3 catalysts. From nitrogen sorption studies, it is also known that insignificant differences in the porous structure of Au/Fe_2O_3 and Au/Fe_2O_3–MO_x catalysts are also not responsible for the change of the activity and stability values. In the reaction the catalysts undergo much sintering, which is most apparent for the TiO_2 modified one, reflected in the surface area and pore volume. XRF element analysis for the examined catalysts did not indicate the presence of any residual Cl^-. Although K^+ residual is assumed to favor increase of activity when the precipitant K_2CO_3 is used instead of Na_2CO_3 [18], the residual is appeared occasionally, which did not account apparently for the change of the catalytic performance. It is noted that the gold contents of the various catalysts increase to some extent for all kinds of the modifying additives and there is no correlation between gold content and WGS activity at the tested reaction temperature. Therefore, it is considered extremely unlikely that the observed WGS activities are due to differences in the gold contents of the various solids. The XRD measurements of the MO_x containing samples did not indicate the presence of crystalline MO or M except for the Cr_2O_3 and Bi_2O_3.The analysis of XRD also showed that, during the thermal treatment of the Au/Fe_2O_3–MO_x samples, the amorphous character of the support was preserved with the exception of the Cu, Cr, Ba, Mo, Bi, Ti, Mn-containing samples. This phenomenon is consistent with the BET surface area. It is worthy noting that the addition of Cr_2O_3 leads

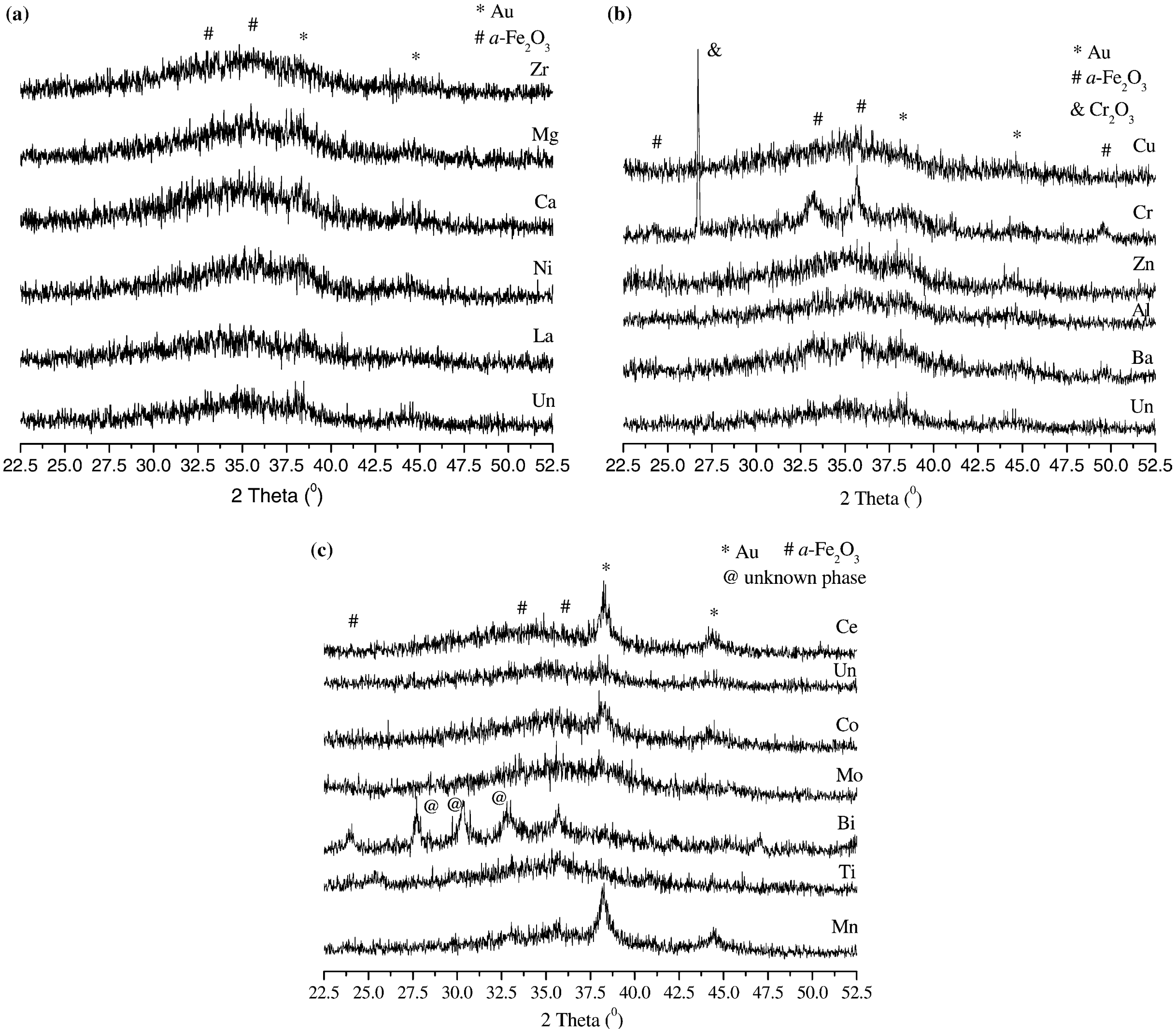

Figure 4. XRD patterns of $Au/Fe_2O_3–MO_x$ catalysts as prepared.

abnormally to easy crystallization of iron oxide and Bi_2O_3 cause the formation of an unknown phase probably due to the high amount of addition. Small amount of introduced Bi_2O_3 can go into the hematite lattice rather than segregate as another phase. Generally, chromium oxide is believed to act as a stabilizer for iron oxide high temperature shift catalyst, retarding sintering and loss of surface area [35]. On the other hand, the dispersion of gold particles on some modified catalysts were altered due to addition of modifying metal oxide. Addings of Ce, Mn, Co, Mo oxides to Au/Fe_2O_3 catalysts could accelerate the congregation of gold particles during calcination step and decrease the dispersion of gold particles. The acceleration is dependent on the nature of the additives, decreasing with the above order. It is noted that for the Au/Al_2O_3 system, results of Centeno et al. showed that ceria would enhance the fixation and final dispersion of gold particles, leading to stabilize them in lower crystallite sizes [29]. Moreover, addition of MoO_3 and MnO_x not only decreased the dispersion of gold particles but also make the support become slightly more crystallized, to a lesser extent for the former. Results of the H_2-TPR studies have confirmed differences in the susceptibility to reduction among the modified Au/Fe_2O_3 catalysts. In other words, the reduction of iron oxide is affected further remarkably due to the addition of the modifying metal oxide. Therefore, it is concluded that additions of modifying additives affect not only the dispersion of gold particles but also the reduction of iron oxide support. This suggests that a direction interaction between gold centers and the modifier, the modifier and the iron oxide, could take place in these solids. This also means that the promotional effects are considered to be responsible for differences in catalytic activities. For the similar systems, Venugopal et al. argued that it is not clear whether the apparent promotional effects are due to some form of direct interaction between gold and the additional element, or whether interaction between the additional element and the iron oxide support are involved [9]. Although we have not conducted detailed examination of reaction activity of the composite supports alone, the

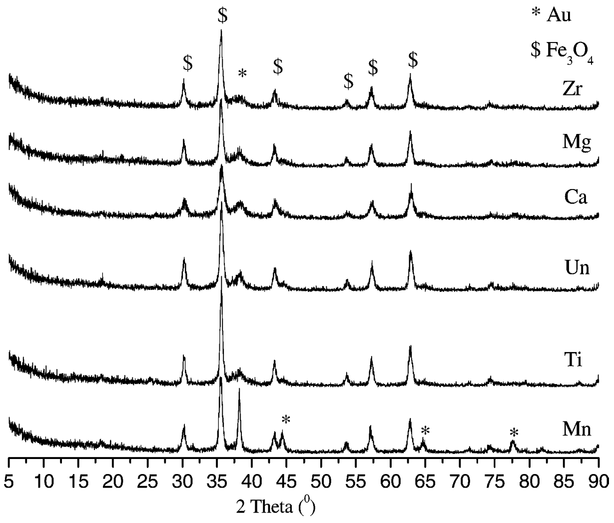

Figure 5. XRD patterns of some Au/Fe_2O_3–MO_x catalysts after WGS reaction.

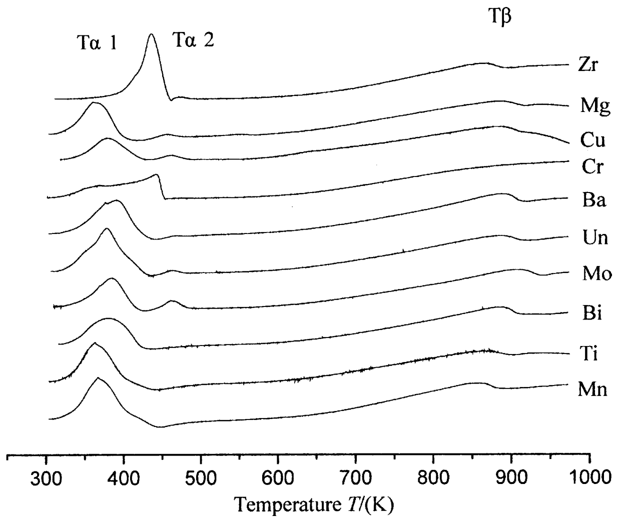

Figure 6. H_2-TPR profiles of Au/Fe_2O_3–MO_x catalysts modified by various metal oxides.

general high initial activity of Au/Fe_2O_3–MO_x catalysts seem unlikely to be only due to the interaction between the additional element and the iron oxide support. It has already been found that just as ZrO_2, the metal oxides, CeO_2, CoO and TiO_2 are very effective supports for gold catalysts, where a very good synergetic effect between could be formed admirably [10,22,31]. However, their additions exert an unsignificant, even detrimental effect on the activity of the correspondingly modified catalyst. Obviously, the variety of activity of the modified catalyst could not be only attributed to the interaction between gold and the modifier, either. Hence in our present work, the various activity of the catalysts is thought to be related to the above two kinds of interaction. Some earlier studies showed that the catalytic performance of Au/Fe_2O_3catalysts prepared through calcination at higher temperature is mainly related to both the dispersion of gold particles and the reduction property of the iron oxide support and contributed to synergistic effects between them [5,22,31,36]. The higher dispersion of gold particles and/or the easier reduction of iron oxide are, the higher activity is. This picture is roughly true for the modified catalysts in our case. The Zr, Mg, Ca, Ni, La, Cu, Cr, Zn, Al, Ba-modified catalysts exhibited higher activities than the unmodified sample and the promotional effect decreased gradually according with the rise of reduction temperature of the iron oxide. For the MoO_3, MnO_X modified Au/Fe_2O_3 catalysts, the decrease of their activity are expected due to the decrease of gold dispersion and uneasy reduction performance of iron oxide. Although the Bi_2O_3-doped catalyst possesses higher dispersion of gold and easy reducibility of iron oxide support, the decreased activity may be due to the formation of unknown phase during calcinations step. Similarly, the CeO_2-modified catalyst holds easier reduction performance than that of the unmodified sample; it showed an activity close to the latter. This maybe explained by the fact that ceria favored the formation of magnetite and decreased the dispersity of gold and these effects compensated each other. However, addition of CoO did not improve the reducibility of support and did decrease the dispersity of gold, the element doped catalyst showed a similar activity with the unmodified sample. On the other hand, the TiO_2 modified catalyst presented gradually decaying catalytic activity, although it holds higher dispersion of gold particles and easier reducibility of the support than that of the unmodified sample. Moreover, the same dispersity and reduction property of the ZrO_2, MgO, CaO modified samples as ZnO modified case did not account for their significant discrepancy in the catalytic performance, either. Comparing the NiO, La_2O_3 modified samples with the Al_2O_3, BaO modifications is in the same picture. From these detailed analysis, it is inferred that the chemical (electronic) effect exerted by modifying additions did contribute considerably to the catalytic performance. Although the influence of modifying additions on the surface electronic state of

Table 6
Peak temperatures of H_2-TPR profiles of Au/Fe_2O_3–MO_x catalysts as prepared

M	Zr	Mg	Ca	Ni	La	Cu	Cr	Zn	Al	Ba	Ce	Un	Co	Mo	Bi	Ti	Mn
$T\alpha 1$/(K)	368	363	366	377	375	381	384	368	375	379	377	391	389	444	382	361	437
$T\alpha 2$/(K)	–	–	–	–	–	–	462	–	–	465	–	469	–	–	462	458	476
$T\beta$/(K)	858	865	844	893	842	885	908	872	973	888	844	890	895	973	883	888	865

supported gold have been confirmed by the studied results of Pestryakov et al. [37], the relative contributions that arise from this probable effect can not been decided presently due to lack of direct results of characterization. It is possible that the some of promoters are incorporated into Fe_3O_4 as a solid solution, in the same way that Cr^{6+} is incorporated into the spinel structure. However, the Fe_3O_4, affected electronically by the modifier element alone, presented unlikely the significant low-temperature activity. It is noted that our results of modification and that reported in the literature are clearly contradictory, probably due to the difference in preparation method, detailed preparation conditions and precipitating agent, *et al.* [31,32].

In addition, just as Au/Fe_2O_3 catalyst, some loss of gold of the modified catalysts occurred during the catalytic operation, regardless of the catalytic performance. Gold loss is unlikely responsible for the different catalytic stability of the Au/Fe_2O_3 catalyst modified by various metal oxides since there is also no relation between WGS activity and gold content of the spent samples. As seen from figure 5, comparing with the unmodified sample, the CaO, MgO, ZrO_2 modified catalysts showed the decreasing FWHM of the magnetite phase and gold, whereas those of the MnO_x modified catalyst apparently became more intense. For the TiO_2 modified case, the patterns of magnetite became more intense while that of gold became weaker instead. Seen from figure 1, the on-line time tested for the studied samples were not consistent exactly. It seems impossible to make exact comparison of XRD results after catalytic operation. However, the CaO, MgO, ZrO_2 modified catalysts remained higher dispersion of gold and more uneasily growing of magnetite crystallites than those of the unmodified sample although they were subjected longer in the catalytic run. In contrary, it is observed for the MnO_x modified catalyst that the congregation of both the gold particles and the magnetite crystallites occurred seriously during catalytic operation in shorter on-line time. Therefore, we can draw a conclusion that the improved stability of the modified gold catalyst is probably related to the preservation of high dispersion of gold particles and uneasily growing of magnetite crystallites during catalytic run. However, it could not be ruled out that the modifying additives could give a considerable effect on the catalytic performance of supported gold catalysts. The results of this study indicate that the electronic effect of modifier on the supported gold catalyst may be a subject worthy of further study.

5. Conclusions

The additions of different metal oxides will exert influence on co-precipitation of gold with iron ion, thus resulting in the fluctuation of gold loading and the content of the additives. But the latter both do not change catalytic activity of the modified Au/Fe_2O_3 catalysts.

Slight change of specific surface and pore structure of catalyst due to the introduction of metal oxide, may not account for the significant difference of the catalytic performance of Au/Fe_2O_3 catalysts, either.

The higher the dispersion of gold particles is, the higher catalytic activity is. The smaller the Fe_2O_3 crystallites are, the easier reduction to Fe_3O_4 is. This is also favorable to increase the catalytic activity. However, the chemical (electronic) effect arising from the modifying element maybe contribute considerably to the enhanced catalytic performance of the supported gold catalyst.

Within the investigated additives, Au/Fe_2O_3 catalyst modified with ZrO_2 shows the highest catalytic activity and stability, while the addition of MnO_x would seriously deactivate the catalytic performance.

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