Redox activity of gold-molybdena catalysts: influence of the preparation methods

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The redox activity of gold-molybdena catalysts, supported on ceria-alumina, prepared by two different methods, was studied. The oxidation activity was measured in complete benzene oxidation reaction. The reduction activity was evaluated by TPR measurements of fresh catalysts and after reoxidation. The influence of the preparation methods is discussed. It was established that two factors were of great importance for the higher redox activity: oxygen mobility and the enhanced electron transfer involving the participation of gold. Both factors depend on the oxygen vacancies formation after adding gold and alumina to ceria as well as on the average size of gold and ceria particles.

Key words: gold-molybdena catalysts, ceria-alumina supports, preparation method, redox activity.

INTRODUCTION

Supported molybdenum oxide catalysts are widely used as catalysts for redox reactions such as propene metathesis [1, 2], ethanol oxidative dehydrogenation [1], propene oxidation [3] methanol oxidation [4, 5], selective partial oxidation of methane [6], *etc*. Recently it was established in our laboratory that $Au-V_2O_5$ and $Au-MoO_x$ catalysts, supported on titania, zirconia, ceria and ceria-alumina were very active at low temperatures in complete benzene oxidation (CBO) [7−10]. It could be assumed that the main factors responsible for the higher activity in CBO are as follows: structure and dispersity of the surface vanadium, resp. molybdenum phase, strength of the V(Mo)=O bond and ease of reduction of the supported $VO_x(MoO_x)$ catalysts. Wachs and co-authors [11, 12] have revealed that the V–O–support bridging bond appears to be controlling the reactivity and reducibility of supported vanadium oxide catalysts. Mestl *et al*. [5] studying MoO_x supported catalysts have suggested that the degree of reduction, and, hence, the presence of reduced surface metal centres, strongly affects the adsorption properties for hydrocarbons, related directly to the reactivity of these catalysts. It was also observed by some of the present authors [13] that a good correlation exists between reducibility and activity of vanadia and molybdena supported catalysts on ceria and titania. Quite recently, it was shown in our laboratory that gold catalysts based on ceria-alumina exhibited a high and stable CBO activity [10]. The addition of alumina to ceria increases the oxygen vacancies concentration and oxygen mobility, which is reflected on the redox activity of this type of catalysts.

The accent in this study is on the relationship between the reducibility and CBO activity of gold-molybdena catalysts supported on ceria-alumina. The influence of the preparation methods on the redox activity is discussed.

EXPERIMENTAL

Catalysts preparation

Two different methods were applied for the preparation of modified ceria support – co-precipitation (CP) and mechano-chemical activation (MA). *Via* the 1st route, ceria-alumina support was synthesized by co-precipitation using nitrates of cerium and aluminium as initial salts in the relevant ratio with a solution of K_2CO_3 (10 wt.% and 20 wt.% of alumina were added, the percentage of alumina is shown after the symbol Al). The supports are denoted as CeAl10CP and CeAl20CP. *Via* the 2nd route, mixed $CeO_2-Al_2O_3$ support was prepared by mechanical mixing of alumina and vacuum dried cerium hydroxide. A mixture of $\gamma-Al_2O_3$ (supplied by BASF, $S_{BET} = 231$ m^2/g) and freshly prepared cerium hydroxide was subjected to mechano-chemical activation by grinding in a mortar for 30 min. The obtained precursor was calcined at 400°C for 2 h. The content of alumina was again 10 and 20 wt.%. Then, before depositing the gold hydroxide, the mixed oxide support was activated in a disintegrator "Ultrasonic UD-20 automatic" under vigorous stirring for 5 min. The supports are denoted as CeAl10MA and CeAl20MA, respectively.

Gold was loaded by the deposition-precipitation method. Deposition of gold on $CeO_2-Al_2O_3$ supports,

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suspended in water, was performed via interaction of $HAuCl_4.3H_2O$ and K_2CO_3 at constant pH = 7.0 and temperature 60°C. After ageing for 1 h, the precipitates were carefully washed, dried in vacuum at 80°C and calcined in air at 400°C for 2 h. The gold loading was 3 wt.%. The syntheses of ceria-alumina and gold catalysts were carried out in a "Contalab" laboratory reactor enabling complete control of the reaction parameters (pH, temperature, stirrer speed, reactant feed flow rate, *etc.*) and high reproducibility.

After deposition of gold, molybdenum was introduced by wet impregnation with $(NH_4)_6Mo_7O_{24}$ solution. The precursors were dried once again under vacuum at 80°C and calcined in air at 400°C for 2 h.

Samples containing only gold or only molybdena were also synthesized. The samples, containing only gold on ceria-alumina were denoted as AuCeAl10CP, AuCeAl20CP, AuCeAl10MA and AuCeAl20MA and the samples, containing only molybdenum – as MoCeAl10CP, MoCeAl20CP, MoCeAl10MA and MoCeAl20MA. The catalysts containing both gold and molybdenum were denoted as AuMoCeAl10CP, AuMoCeAl20CP, AuMoCeAl10MA and AuMoCeAl20MA.

The all used initial salts were of "analytical grade" of purity.

Catalytic activity

The catalytic activity was expressed as a degree of benzene conversion. It was measured using microcatalytic continuous flow fixed-bed reactor at atmospheric pressure, connected to a "Perkin Elmer" gas chromatograph, equipped with a flame ionization detector (2 m column filled with Porapak Q at 65°C). Benzene was fed into the catalytic reactor using air as carrier gas through a benzene saturator, which was kept at an appropriate temperature to maintain the desired benzene concentration. The oxygen to benzene ratio was about 7.5 (the stoichiometric ratio) needed for complete benzene oxidation. The following conditions were chosen: catalyst bed volume 0.5 cm^3 (particle size 0.25−0.50 mm), inlet benzene concentration 4.2 g·m^{-3} in air, space velocity 4000 h^{-1}, temperature range 150−300°C. The catalyst amounts charged into the reactor and the catalysts particles size were selected to be small enough to avoid both bulk and pore diffusion retardation effects. The samples were activated "*in situ*" by purified air at 150°C for 1h. A special experiment with supplementary chromatographic analysis was carried out with a column Carbowax 20M HPDMCS. No byproducts of mild oxidation were registered.

TPR measurements

The TPR measurements were carried out by means of an apparatus described elsewhere [14]. A cooling trap (−40°C) for removing the water formed during reduction was mounted in the gas line prior to the thermal conductivity detector. A hydrogen-argon mixture (10% H_2), dried over a molecular sieve 5A (−40°C), was used to reduce the samples at a flow rate of 24 ml·min^{-1}. The temperature was lineally raised at a rate of 15°C·min^{-1}. The sample mass charged was 0.05 g. The amount was selected based on the criterion proposed by Monti and Baiker [15]. In addition, TPR experiments were performed after re-oxidation. The reoxidation with purified air was carried out at two different temperatures. In the first case of high temperature (HT) re-oxidation the H_2-Ar flow was discontinued and air was fed at the temperature immediately after the end of the corresponding TPR peak of the fresh sample. The sample was kept in air at this temperature for 15 min and then the TPR profile was recorded after cooling down to room temperature (RT) in purified argon flow. In the second case after the end of the TPR peak the sample was cooled down in purified argon flow to RT, reoxidized in air for 15 min and then the TPR pattern was registered (RT reoxidation).

Hydrogen consumption (HC) during the reduction processes was calculated using preliminary calibration of the thermal conductivity detector, performed by reducing different amounts of NiO to Ni (NiO "analytical grade" of purity, calcined for 2 h at 800°C to avoid the presence of non-stoichiometric oxygen).

RESULTS

The chemical composition, BET surface area and average size of gold and ceria particles of the gold-containing samples and the initial supports are presented in Table 1. The introduction of gold and alumina causes an increase in the BET specific surface area. The average size of gold particles, determined by XRD measurements, is below 6 nm [10]. In MA samples, the average size of gold is smaller than that in the CP ones. For the ceria particles size the opposite tendency was observed. For the MA samples, the average size of ceria particles was higher than that for the CP catalysts. The addition of alumina led to an increase in the number of oxygen vacancies, estimated by the main line of ceria in Raman spectra [10].

TPR results

The reduction behaviour of the studied samples was evaluated by TPR measurements. The hydrogen

consumption was calculated as well.

Table 1. Chemical composition, BET surface area and average size of Au and CeO_2 particles of the gold-based catalysts and initial supports.

Catalysts	Au content	MoO_3 content	BET surface area	Average size	
				Au	CeO_2
	wt. %	wt. %	$m^2 \cdot g^{-1}$	nm	nm
CeAl10CP	-	-	83	-	5.0
CeAl20CP	-	-	83	-	4.5
CeAl10MA	-	-	89	-	9.5
CeAl20MA	3.0	-	98	-	9.2
AuCeAl10CP	2.9	-	103	4.0	4.0
AuCeAl20CP	3.0	-	140	6.0	3.0
AuCeAl10MA	3.0	-	105	2.9	10.0
AuCeAl20MA	3.0	-	115	3.5	9.7
AuMoCeAl10CP	2.9	4.0	110	4.0	4.0
AuMoCeAl20CP	3.0	4.0	123	6.0	3.0
AuMoCeAl10MA	3.0	4.0	87	2.9	10.0
AuMoCeAl20MA	3.0	4.0	98	3.5	9.7

Figure 1 represents the TPR profiles of gold containing CP catalysts. Only the low temperature (LT) region is represented because only it is of interest for the studied catalytic reaction. The TPR profiles of the initial supports are shown as inset. Two peaks have been registered in the TPR pattern of pure ceria: a high temperature (HT) peak at T_{max} = 855°C, connected with the bulk reduction of ceria and a LT one at T_{max} = 490°C, assigned to the ceria surface layers reduction [16]. In the profiles of both ceria-alumina supports only one peak (T_{max} = 535°C for the CeAl10 sample and T_{max} within the interval 500−550°C for the CeAl20 sample) was registered in the region up to 800°C. For all gold-containing samples a significant lowering of the temperature of ceria surface layers reduction was observed as in a previous study [17].
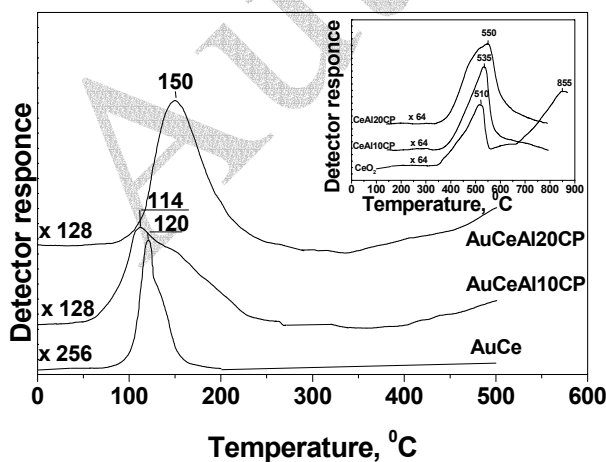
The TPR patterns of gold-molybdena containing catalysts are shown in Fig. 2, as insets are presented the TPR profiles of samples containing only molybdena. The T_{max} of the peak, assigned to the molybdena and ceria reduction, had the lowest value for the MoCe sample (487°C). The peak with the highest T_{max} (517°C) as well as the highest intensity was observed with the MoCeAl20CP sample. The LT-TPR peaks of gold-molybdena catalysts were located at temperatures about 300° lower than those of the corresponding non-containing gold samples. These peaks are obviously complex due both to ceria surface layers and to MoO_x species reduction. The peak of the AuMoCe sample is a narrow one with a predominant LT part at T_{max} = 120°C and a HT shoulder at about 180°C, assigned to the MoO_x reduction. The peaks of the samples on mixed ceria-alumina supports are broad ones with T_{max} within the interval 120−220°C.
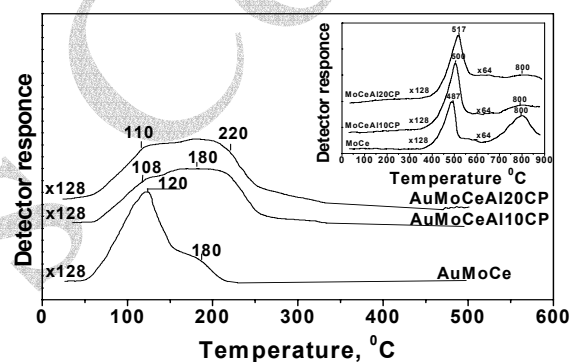

Fig. 2. TPR spectra of gold-molybdena catalysts; inset: molybdena samples.

The TPR patterns of gold-containing samples MA, nonpromoted and promoted by molybdena are represented in Fig. 3, as insets are given the TPR profiles of the initial supports MA.
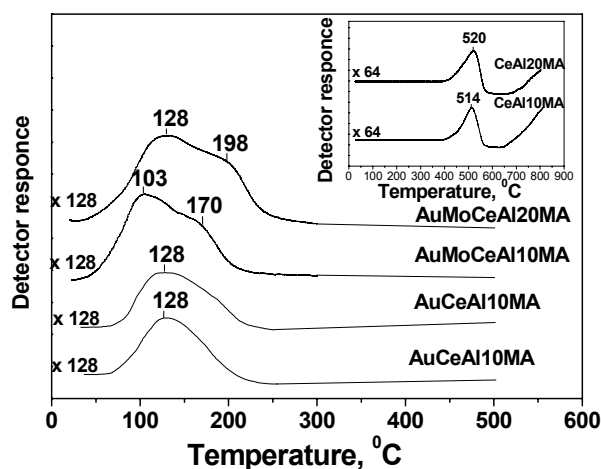

Fig. 3. TPR spectra of the gold-based and gold-molybdena catalysts; inset: initial supports.

Fig. 1. TPR spectra of the gold-based catalysts; inset: initial supports.

For the pure supports, in the region up to 800°C peaks with T_{max} = 514°C for the CeAl10MA, respectively 520°C for the CeAl20MA, were registered, related with the surface layers reduction. The start of the second HT peak is also visible. The addition of gold leads again to a significant shift of the reduction temperature of ceria surface layers to the LT region. For both AuCeAl10MA and AuCeAl20MA samples the reduction peaks are at T_{max} = 128°C and they are very similar, independently of the alumina content. T_{max} in the TPR peaks in the case of MA samples are generally a little bit higher than those of the CP samples.

Additional experiments on reoxidation of the catalysts after the direct TPR were carried out. The reoxidation was accomplished at RT as well as at HT. The TPR profiles of gold-containing CP samples after RT and HT reoxidation are represented in Fig. 4: nonpromoted (Fig. 4A) and promoted by molybdena (Fig. 4B). For gold-molybdena CP catalysts on mixed supports the HC at RT and especially at HT (the temperatures at the end of the TPR peak of the fresh samples, which are practically equal to the reaction temperatures for the highest benzene conversion degree) is very close to that of the initial samples.
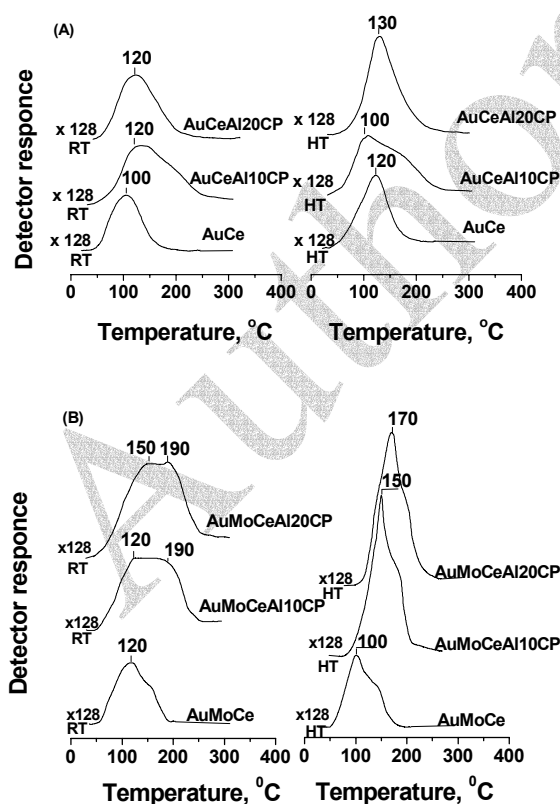

Fig. 4. TPR spectra after RT and HT reoxidation of: A − gold catalysts and B – gold-molybdena catalysts.

For the gold-containing MA samples the TPR

profiles after reoxidation are given in Fig. 5A and for the gold-molybdena MA catalysts in Fig. 5B. After reoxidation at RT, T_{max} for the ceria-alumina based MA catalysts was shifted to higher temperatures, but after reoxidation at HT, the temperature of the peak maximum was shifted to the LT region – for the AuCeAl10MA sample T_{max} = 80°C and for the AuCeAl20MA – T_{max} = 97°C. The addition of molybdena causes differences in the form and position of the LT TPR peaks. They are complex and are attributed to the reduction of molybdena surface layers as well as of the ceria surface layers. It is interesting to note that after HT reoxidation (the temperature region of the catalytic reaction), the LT shoulder, which we attributed to the reduction of ceria surface layers, was disposed at temperatures higher than those for the samples nonpromoted by molybdena.
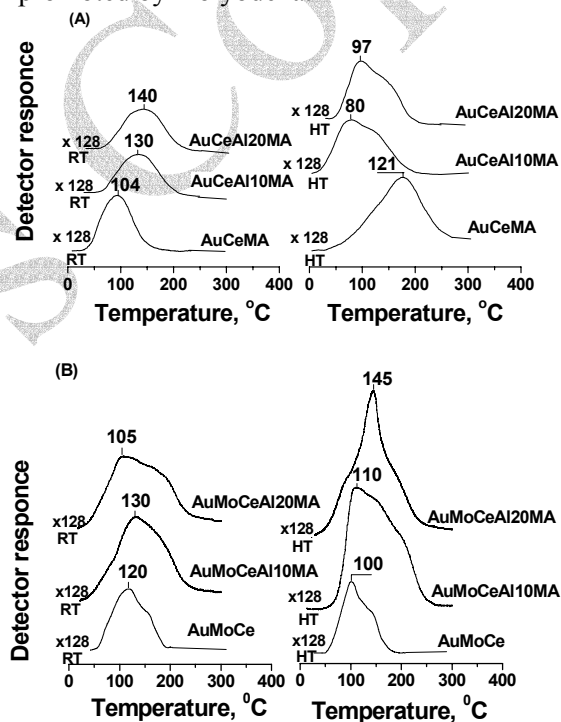

Fig. 5. TPR spectra after RT and HT reoxidation of: A − gold catalysts and B – gold-molybdena catalysts.

In Table 2 the hydrogen consumption corresponding to the first LT-TPR peak of the studied catalysts is presented. Comparing the initial supports CP and MA, big differences are visible due to the different methods of preparation. It is seen that the hydrogen consumption of the pure supports CP in the presence of alumina is significantly higher compared to that of MA samples and pure ceria. The H_2 consumption of the CeAl20CP sample is the highest. This behaviour could be connected with the enhanced reduction of deeper ceria layers, due to the oxygen vacancies formation in the presence of alumina.

Table 2. Hydrogen consumption to the first TPR peak in the spectrum of the fresh catalysts and after reoxidation at room temperature (RT) and at high temperature (HT).

Sample	HC of direct TPR, $\mu mol \cdot g^{-1}$	HC after RT reoxidation, $\mu mol \cdot g^{-1}$	HC after HT reoxidation, $\mu mol \cdot g^{-1}$
Ce	492	-	-
CeAl10CP	716	-	-
CeAl20CP	1006	-	-
CeAl10MA	299	-	-
CeAl20MA	352	-	-
AuCe	462	240	300
AuCeAl10CP	528	360	360
AuCeAl20CP	572	320	400
AuCeAl10MA	352	216	322
AuCeAl20MA	322	216	334
AuMoCe	550	260	270
AuMoCeAl10CP	570	510	540
AuMoCeAl20CP	730	550	720
AuMoCeAl10MA	422	476	594
AuMoCeAl20MA	458	470	562

After RT or HT reoxidation, the oxygen capacity of the fresh CP catalysts containing gold only cannot be reached. In the case of AuMoCe the oxygen treatment at RT and HT is also not enough to restore the oxygen capacity of the fresh sample. Upon adding molybdena some supplementary amount of hydrogen, corresponding to the reduction of MoO_x species, was consumed. Comparison between gold-molybdena containing catalysts shows that the same tendency is reproduced (higher H_2 consumption in the presence of Al^{3+}). In the latter case the peaks are less intensive because they are located at significantly lower temperatures, at which the oxygen mobility is not so high, compared to that of the catalysts without gold. For the MA samples containing only gold, after reoxidation at RT the oxygen capacity did not reach the initial value, but upon reoxidation at HT, the hydrogen consumption of the AuCeAl20MA sample was even higher. On the contrary, the hydrogen consumption was higher with the Au-Mo samples even at RT and the oxygen capacity was fully recovered.

Catalytic activity data

The catalytic activity of the samples was estimated in the reaction of complete oxidation of benzene and the benzene conversion was taken as a measure of it. The results on the temperature dependence of the catalytic activity of the CP samples are represented in Fig. 6. The catalysts containing molybdena show a significantly lower activity in this temperature interval (not shown in the figure). Generally, the catalysts supported on CeAl20CP are more active than the corresponding catalysts on CeAl10CP. In the LT region the activity

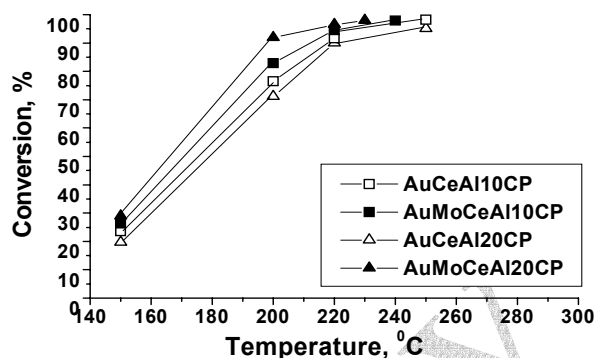is low and there are practically no significant differences.

Fig. 6. Temperature dependence of the catalytic activity in CBO of the catalysts studied.

The catalytic behaviour of the MA samples is quite different compared to the CP samples. The catalytic activity data on the corresponding gold samples, supported on CeAl10MA and CeAl20MA, nonpromoted and promoted by molybdena are compared in Fig. 7, A and B.
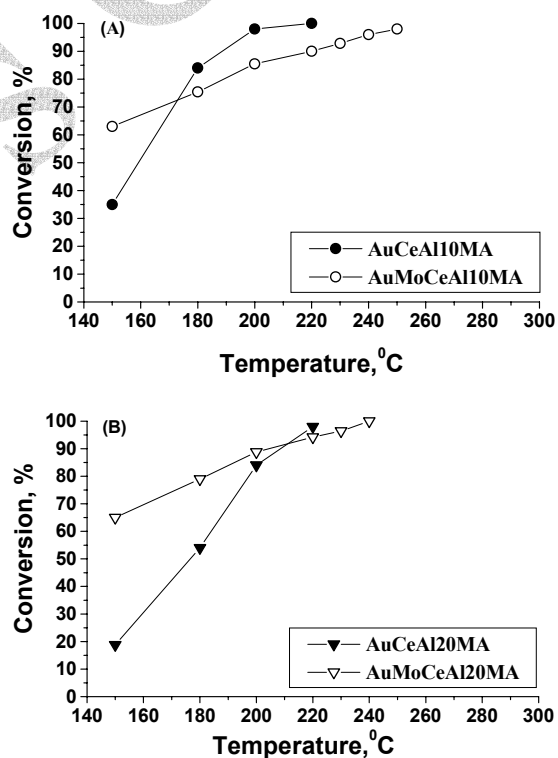

Fig. 7. Temperature dependence of the CBO conversion degree on the catalysts: (A) containing 10 wt. % alumina and (B) containing 20wt. % alumina.

An interesting catalytic behaviour is observed. The gold catalysts promoted by molybdena exhibit a higher activity in comparison to the corresponding nonpromoted ones in the LT interval. At the higher temperatures the opposite behaviour is observed.

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Depending on the alumina content, the temperature of the cross-point of the two activity curves is different. This temperature is higher for the sample with higher alumina content. The catalysts containing molybdena showed a significantly lower activity (not shown in Fig.) than that of other catalysts and they will not be an object of further discussion. For the gold MA samples higher activities are exhibited by the AuCeAl10MA sample but at 220°C the activities of gold samples containing 10 and 20% alumina are practically equal (at about 100% conversion). This tendency is reversed for the gold-molybdena samples. The activity in the LT region of the samples containing Au-Mo is higher than that of the samples containing only gold. In the whole temperature range, a slightly higher activity was manifested by the AuMoCeAl20MA catalyst than that of AuMoCeAl10MA.

In Fig. 8 the catalytic activities of the Au-Mo samples, obtained by both preparation methods are compared: for the samples, containing 10 wt.% of alumina (A) and for the samples, containing 20 wt.% of alumina (B). One can see that in the LT region the MA catalysts are more active, while in the HT region the activities are almost equal, a slightly higher being that of the CP ones.
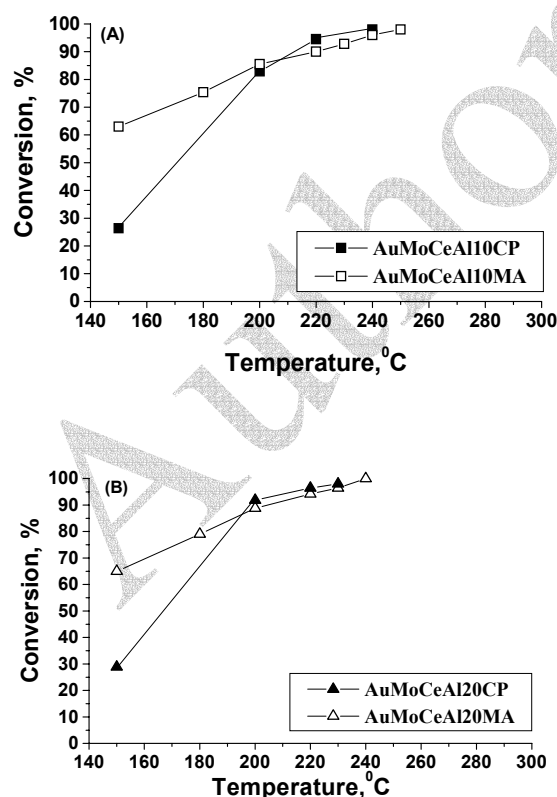

Fig. 8. Temperature dependence of the CBO conversion degree on the gold-molybdena catalysts: (A) containing 10 wt.% alumina and (B) containing 20 wt.% alumina.

DISCUSSION

The obtained catalytic activity data showed different behaviour depending on the applied method of preparation. The MA catalysts containing simultaneously gold and molybdena are more active in the LT interval than the corresponding CP catalysts. In the HT region the opposite behaviour was found out. The MA catalysts, containing only gold were more active in the HT region compared to the gold-molybdena MA samples. The cross-point position depended on the alumina content.

The studied catalytic systems are complicated and more than one factors are of great importance for the higher redox activity. On one hand, this is the oxygen mobility, which is enhanced by the presence of oxygen vacancies. On the other hand is the electron transfer from the hydrocarbon to the oxygen molecule via the catalytic surface by the activation of hydrocarbon on MoO_x species being able to enhance the redox transfer. The activation of hydrocarbons at temperatures below 220°C is possible only in the presence of gold. The electron transfer also proceeds between small gold particles and Ce^{3+} ions via oxygen vacancies and depends strongly on the size of gold particles [10, 18]. The transfer becomes possible due to the strong modification of ceria in the presence of gold [19]. Studying the reaction mechanism by FTIR of CBO on $Au-V_2O_5$ supported on titania it was found out, that the activation of benzene took place on the VO_x species [20]. The MoO_x species should play the same role like that of VO_x in gold-vanadia supported catalysts. The addition of gold to the catalysts in all cases leads to a significant lowering of the reduction temperature of ceria surface layers, which is in accordance with the higher LT redox activity of the gold catalysts.

Concerning Au and Au-Mo MA catalysts, the temperature of the cross-point should be around the point, where the predominant role of the first factor gives away to the role of the second one.

The enhanced oxygen mobility upon adding alumina to ceria is seen very well comparing the HC during TPR of the initial supports prepared by CP. In this case the first peaks in the TPR profiles of the samples are due not only to the ceria surface layers reduction, but also to the reduction of deeper layers. The calculated degree of reduction for CeAl10CP is 27.4% and for CeAl20CP, 43.3% [21]. Sanchez and Gazquez have considered that CeO_2 can be reduced up to 17% without changing the fluorite structure to the hexagonal Ce_2O_3 structure [22]. Laachir and coworkers have observed that when the reduction is limited only to the surface of ceria, this leads to a

20% reduction degree [23]. In view of these observations, the bulk reduction of ceria-alumina samples, leading to structural changes, has to be considered. The bulk ceria reduction is stronger when the amount of alumina is higher. This enhancement of ceria reduction can be connected with increased oxygen mobility in the defective ceria structure generated by the introduction of alumina using the CP method of preparation. In addition, the reduction process is enhanced by the decrease of the size of metal oxide particles. For the CP catalysts the addition of alumina leads to the lowering of the average size of ceria particles (about 2 times) [10]. In the case of MA technique (Table 2), the HC is lower than that of pure ceria. This means that only surface ceria layers are reduced, which could be related to the predominant vacancies formation on the catalysts surface. The increase of alumina amount leads to the higher HC for both preparation methods. However, the differences in the case of CP between 10 and 20% alumina are drastic due to the creation of deep oxygen vacancies at higher concentration.

In all cases the addition of gold leads to a significant lowering of the reduction temperature of ceria surface layers. This effect is related to the hydrogen activation on nanosized gold particles [24] and an increase in number of potential sites for reduction along the border between gold and support. Additionally, the introduction of alumina leads to an enhancement of ceria reduction, connected to the oxygen mobility in the defective ceria structure. After reoxidation at RT and at HT for gold-containing samples, the redox capacity was partially recovered. Comparing the HC of the gold-containing samples in the LT region, it can be seen that the higher HC was registered with the CP samples compared to the MA ones. This is in accordance with the higher concentration of oxygen vacancies, found by Raman spectroscopy [10]. It has to be noted that after reoxidation at HT (the temperature of the catalytic reaction) the oxygen capacity of CP samples cannot be recovered, while in the case of MA catalysts almost the same oxygen capacity as in the fresh samples was restored (Table 2).

In the presence of molybdena as a promoter, a complex TPR peak was registered in the LT region due to the reduction of both ceria surface layers and MoO_x species. Modifying ceria by alumina, a broadening of the LT TPR peaks was additionally found. The TPR results after reoxidation at HT show that for both preparation methods the recovering of the oxygen capacity is complete in the presence of molybdena. After RT reoxidation only for the MA catalysts the HC is even higher than that of the fresh samples, which is fully in agreement with the higher LT activity of Au-Mo MA samples. This is also in accordance with the higher dispersion of gold in the MA catalysts (2−3 nm compared to the CP ones, 4−6 nm) [10]. Another explanation is the lower surface at.% of Au for the CP catalysts compared to the MA samples, estimated by XPS measurement results (0.30 at.% for AuMoCeAl10CP and 0.16 at.% for AuMoCeAl20CP compared to 0.41 at.% for AuMoCeAl10MA and 0.37 at.% for AuMoCeAl20MA) [10]. In the HT region (200°C and higher) the catalytic activities are almost independent of the preparation methods, the CP catalysts exhibit even a slightly higher activity than the MA ones, most probably due to the higher oxygen mobility. This is valid for the samples with 10 wt.% alumina as well as for those with 20 wt.% (Fig. 8).

CONCLUSIONS

The study of complex catalytic systems based on Au-Mo supported on ceria-alumina showed that more than one factor influenced the CBO activity. In the LT region the effect of electron transfer with the participation of nanosized gold particles has a prevailing effect and this is in agreement with significantly higher activity of Au-Mo MA samples. In the HT region obviously a predominant role is played by the oxygen mobility, related to the presence of oxygen vacancies. It could be concluded that redox activity depends on one hand on the reaction temperature and on the other hand on the method of catalysts preparation.

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РЕДОКС АКТИВНОСТ НА ЗЛАТО-МОЛИБДЕНОВИ КАТАЛИЗАТОРИ: ВЛИЯНИЕ НА МЕТОДИТЕ НА ПОЛУЧАВАНЕ

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(Резюме)

Изучена е редокс активността на злато-молибденови катализатори, нанесени върху цериев диоксид-алуминиев оксид, получени по два различни метода. Окислителната активност на катализаторите е измерена в реакцията на пълно окисление на бензен. Редукционната активност е оценена с помощта на ТПР измервания на свежи катализатори и след реокисление. Дискутирано е влиянието на метода на получаване върху редокс активността. Установено е, че главно два фактора са от съществено значение за високата редокс активност на катализаторите: кислородната мобилност и улеснения пренос на електронна плътност с участието на златото. Двата фактора зависят от степента на формиране на кислородни ваканции след добавката на злато и алуминиев оксид към цериевия диоксид, както и от размера на златните и цериевооксидните частици.