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CO hydrogenation over Al_2O_3: pseudo-hydrothermal and basic alkali metal compounds pretreatment effect

Wenzhong Zhang, Hua Yang, Guiqin Su, Runxiong Gao and Yuanqi Yin [1]

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

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Aluminas pretreated with pure water (pseudo-hydrothermal treatment) and very dilute basic aqueous solutions were used as catalysts for CO hydrogenation. Pseudo-hydrothermal treatment results in an apparent enhancement of ethylene selectivity at elevated temperature (>673 K). The active sites seem to be coordinatively unsaturated metal and oxygen counter-ions (Lewis acid and base pair), which are very probably located on the most external surface of the alumina and can be coordinatively saturated by calcination in air. The precursors of the active sites probably originate from a very thin layer of boehmite beyond XRD detecting ability. They can be generated by both pseudo-hydrothermal treatment and dilute basic aqueous solution treatment of alumina.

Keywords: alumina; CO hydrogenation; ethylene

1. Introduction

The effects of metal oxides on the catalytic properties of transition metals have been the subject of considerable discussions in the literature. Burch [1], Sachtler and co-workers [2,3], Bell, Somorjai and co-workers [4] suggested the enhancement of CO hydrogenation could be attributed to the formation of a Lewis acid–base complex between the oxygen end of adsorbed CO and the metal ion. The promotion of the metal by the oxide occurred only at the boundary between the oxide and the metal. However, the behaviors of AlOx on decoration of Rh foil for CO hydrogenation to methane were different from those of other metal oxide species [4]. This difference probably indicates that alumina possesses some unique property for CO hydrogenation. Although much more knowledge has been published for metal–metal oxide systems, we still know very little about the pure metal oxide as catalyst for CO hydrogenation. Our previous study [5] shows that pretreated alumina

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[1] To whom correspondence should be addressed.

favors production of ethylene rather than methane at adequate temperature. Thus, alumina deserves further study.

In our previous paper [5], it has been reported that both the conversion of CO and the selectivity of light olefins are promoted by the pretreatment of Al_2O_3 with an aqueous solution of sodium acetate. The promotion effects were discussed in terms of acidic and basic sites produced at the interface of boehmite and bulk alumina at elevated temperature. However, these sites are neither sensitive to air nor to calcination in air. This leads to the question: if the active sites are located at the most external surface of alumina rather than at the interface of two phases, what will their catalytic activity for CO hydrogenation be. It was expected that such samples could be prepared by using dilute basic aqueous solutions, so very dilute solutions (0.02 mol/ℓ) of NaOH, KOH, LiOH, K_2CO_3 and pure H_2O were used to pretreat alumina. The catalytic results showed that CO conversion and olefin selectivity increased after pretreatment; however, the activity and olefin selectivity of these pretreated catalysts decreased significantly after several days of exposure to air or calcination in air. These results were discussed in relation to the formation of a coordinatively unsaturated pair of counterions on the most external surface of the samples which could easily be attacked by foreign reagents in air, such as O_2 and CO_2, leading to saturation and the elimination of active sites, thereby decreasing CO conversion and olefin selectivity.

2. Experimental

Two gamma type aluminas without XRD detectable boehmite phase from different sources were used: one the same as used in our previous paper [5], 208, from Wenzhou Chemicals, denoted by W208, the other one from Qindao Chemicals (China), denoted by Q198. Both have a surface area of about 170 m^2/g. The XRD patterns of these two samples are almost the same, as can be found in our previous paper [5]. The impurities in them predominantly consist of sodium and iron, but iron cannot be detected by means of XPS. Q198 has slightly more sodium (about 10 ppm more) than W208. The iron content is less than 10 ppm according to ICP atomic emission analysis. In order to exclude the contribution of possibly contaminated transition metals to the catalytic activity, 10 ppm of different transition metals, such as Fe, Mn, Ru, Co and Ni, were introduced to the alumina through impregnation of the corresponding nitrates. The resultant samples were calcined and reduced at 723 K for 4 h before the catalytic reaction run. The results indicate CO conversion increased apparently but olefin selectivity decreased significantly.

Pseudo-hydrothermal treatment of alumina was carried out as follows. 20 g of each alumina was washed five times with deionized water. The washed sample was added to 100 ml of deionized water in a beaker which was heated on an oven until all the water was vaporized. Then the sample was kept in a desiccator until use. Alumina pretreated with basic alkali metal compounds was prepared as follows. 18 g of each alumina was refluxed in 500 ml of a 0.02 mol/ℓ solution of each of the alkali compounds at 373 K for 8 h. Samples were obtained after filtering and washing thoroughly. These samples were kept in a desiccator too.

Catalytic CO hydrogenation was carried out in a stainless steel fixed bed reactor with 2.0 ml of catalyst with particle size of 20–60 mesh under the following conditions: 1.0 MPa syngas with a H_2/CO ratio of 3, space velocity of 600 h^{-1} and a wide range of temperatures from 573 to 723 K. An on-line gas chromatograph with FID and capillary column was used for hydrocarbon analysis. Details of these experiments can be found elsewhere [5]. The CO conversion was calculated by carbon balance. The selectivity to each hydrocarbon was calculated by normalizing all the hydrocarbons formed.

3. Results and discussion

Table 1 shows that CO hydrogenation on both Q198 and W208 before and after pseudo-hydrothermal treatment gives apparently different results. Due to the low conversion level on these alumina catalysts, it is necessary to emphasize that almost identical results on the same catalyst in different sets of measurements were obtained. CO conversion is increased accompanied by a decrease of methane selectivity after the treatment on both aluminas. The formation of C_2 and C_3 olefins seems to be enhanced on W208; however, it was almost unchanged on Q198 according to the O/P ratio. Actually, figs. 1 and 2 show that ethylene selectivity on both aluminas increases almost linearly with temperature above 623 K (this behavior is similar to that of the alumina pretreated with sodium acetate [5]). In fact, the selectivity of propene is also improved after treatment, but the improvement is not very obvious on both aluminas. Figs. 3 and 4 show that methane formation on both aluminas is apparently suppressed by pseudo-hydrothermal pretreatment. The suppression becomes more intense when the temperature rises up to 673 K. This

Table 1
Pseudo-hydrothermal pretreatment effect on activity and selectivity of CO hydrogenation over alumina [a]

	Pretreatment	C_1	C_2	C_3	C_4	O/P [b]	CO conv. (%)
Q198	none	51.2	27.6	11.8	9.4	0.89	2.4
	H_2O	39.0	32.7	15.7	12.6	0.87	4.3
	723 K [c]	71.8	16.7	7.9	3.6	0.83	2.8
W208	none	69.9	18.3	8.8	2.9	0.64	1.0
	H_2O	55.6	28.0	11.8	0.9	0.84	1.7
	723 K [c]	83.7	11.1	3.6	1.6	0.73	1.4

[a] The reaction temperature is 623 K.
[b] O/P is the ratio of the sum of C_2 and C_3 olefins to total C_2 and C_3 hydrocarbons.
[c] The alumina pretreated with H_2O was calcined in air at 773 K for 3 h.

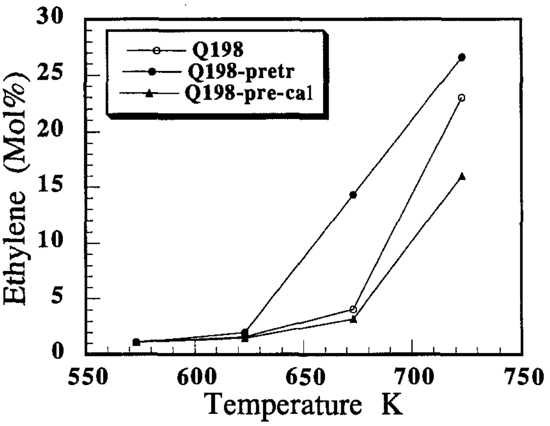

Fig. 1. Ethylene selectivity versus reaction temperature on alumina (Q198); alumina pretreated with pseudo-hydrothermal method (Q198-pretr); pretreated alumina calcined at 773 K (Q198-pre-cal).

suppression took place along with the increase of ethylene selectivity (figs. 1 and 2). In addition, the active sites formed at elevated temperature in syngas after pseudo-treatment seemed not stable to calcination in air because CO conversion, olefin to paraffin ratio and ethylene selectivity all decreased, the methane formation was no longer suppressed, and even more methane was produced after calcination in air. These results observed on both aluminas indicate that the pseudo-hydrothermal pretreatment effect is not a fortuitous phenomenon. It has been demonstrated in the literature [6,7] that boehmite could be produced by hydrothermal treatment even by "alcohol thermal" treatment of gibbsite, an alumina analog. In addition, both Bond's [8] and our previous papers have verified that boehmite can be easily generated by treatment of alumina with weak basic sodium acetate

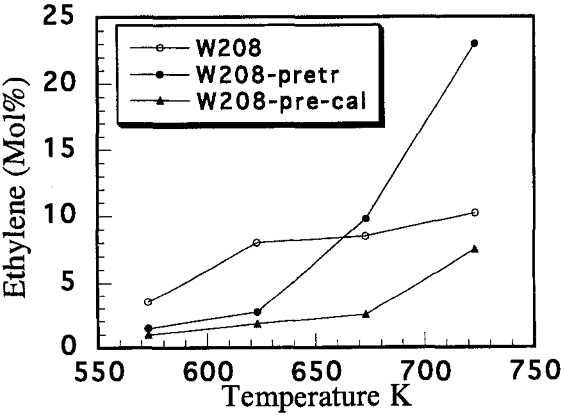

Fig. 2. Ethylene selectivity versus reaction temperature on alumina (W208); alumina pretreated with pseudo-hydrothermal method (W208-pretr); pretreated alumina calcined at 773 K (W208-pre-cal).

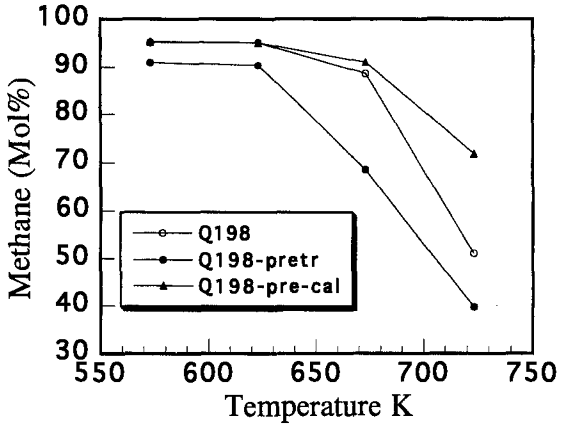

Fig. 3. Methane selectivity versus reaction temperature on alumina (Q198); alumina pretreated with pseudo-hydrothermal method (Q198-pretr); pretreated alumina calcined at 773 K (Q198-pre-cal).

solution through simple refluxing. Therefore, as a result of pseudo-hydrothermal treatment, a very thin layer of boehmite has probably formed on the most external surface of the alumina and is beyond XRD detecting ability. The explanation given in our previous paper may be also suitable here. Boehmite serves as the precursor of Lewis acidic and basic sites which are coordinatively unsaturated metal ions and oxygen anions formed through dehydroxylation of boehmite at elevated temperature [5]. Compared with the positive effect of calcination obtained before [5], the negative effect of calcination here probably reveals that the precursors of active sites formed during treatment are located at the most external surface of alumina instead of between the boehmite and bulk alumina; therefore, these sites are unstable. After formation they will be easily accessible to oxygen and be coordina-

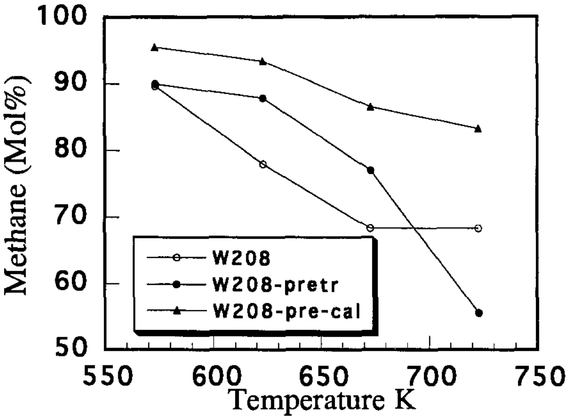

Fig. 4. Methane selectivity versus reaction temperature on alumina (W208); alumina pretreated with pseudo-hydrothermal method (W208-pretr); pretreated alumina calcined at 773 K (W208-pre-cal).

tively saturated to the energy permissible extent during calcination in air. Transformation of active metastable sites to stable inactive sites takes place, thereby decreasing the catalytic activity and selectivity.

As described previously, the formation of boehmite is most important for active sites generation on alumina. Weak base treatment (NaOAC) has been illustrated to be a good conventional approach [5,8]. A series of alkali metal compounds such as LiOH, NaOH, KOH, and K_2CO_3 were used to treat W208 for comparison. The results of CO hydrogenation are listed in table 2. It is interesting that potassium, which usually promotes many metal catalysts to produce more olefin from CO hydrogenation, has no positive promoting effect here. Thus, it supports additionally that the activity of alumina cannot be assigned to trace amounts of iron in these two aluminas. The behavior of W208 after most of these treatments is somehow different either from that after pseudo-hydrothermal treatment or from that after sodium acetate pretreatment, except in the case of pretreatment with NaOH [5]. No linear increase of ethylene selectivity with temperature was observed. Only slight increases of CO conversion and O/P ratio were obtained. Among these compounds sodium hydroxide is the best for promotion of CO conversion and olefin selectivity, especially ethylene selectivity which increases linearly with reaction temperature. The XRD pattern of alumina after these treatments shows that no new phase is formed. However, it has been approved that boehmite could be formed after treatment of W208 with a higher concentration of NaOH aqueous solution (i.e. 0.1 M instead of 0.02 M). These results indicate that the change of CO hydrogenation behavior of W208 might be due to changes in local environment of the most external surface of the sample. In the cases of KOH, K_2CO_3 and LiOH, a very high possibility for the formation of a very thin layer of boehmite exists as in the case of NaOH, because their dilute aqueous solution possesses similar basic properties. Logically, let us first assume that a very thin layer of boehmite was formed and the coordinatively unsaturated metal ions and oxygen anions were also producible at elevated temperature in syngas, but the pair of coordinatively unsaturated counterions were coordinated by potassium or lithium oxide species with the oxy-

Table 2
CO hydrogenation activity and hydrocarbon selectivity on W208 pretreated by using various basic alkali compounds [a]

Compound	C_1	C_2	C_3	C_4	O/P	CO conv. (%)
LiOH	74.4	16.2	6.5	2.9	0.69	1.3
NaOH	61.1	24.2	9.4	5.3	0.81	2.4
	(84.5)	(11.0)	(2.8)	(1.7)	(0.57)	(0.99)
KOH	80.5	12.6	4.3	2.6	0.67	1.2
K_2CO_3	64.4	20.7	9.6	5.9	0.78	1.9
none	69.9	18.3	8.8	2.9	0.64	1.0

[a] See table 1 for reaction conditions and notes. The data in parentheses are the results obtained on W208 pretreated with NaOH and calcined in air at 773 K for 3 h.

gen end toward the metal ion and the alkali ion end toward the oxygen anion, thus poisoning both the acidic and basic sites. This can explain the negative promotion effect for CO hydrogenation. The different promotion ability of NaOH from that of KOH and LiOH needs further study. However, it may be due to the different basicity they possess: potassium oxide species exhibit the strongest basicity; sodium oxide species exhibit an intermediate basicity. As a logical result, residual potassium oxide species on alumina (cannot be washed) favor coordination to stronger Lewis acid sites than sodium oxide species; however, residual lithium oxide species favor coordination to weaker Lewis acid sites. Thus both of them possess a higher possibility to make the meta-stable active sites deviate from the optimized condition for CO hydrogenation. This can be further confirmed by the fact that KOH with a stronger basicity has a lower promotion ability than K_2CO_3 with a weaker basicity. The different CO hydrogenation results between Q198 and W208 also reveal that residual sodium has a certain kind of promotion effect on alumina because no other differences can be found except the slight difference in sodium content.

The data in parentheses of table 2 reveal that active sites formed after basic solution treatment are sensitive to calcination in air too. Therefore, as we expected, the active sites for CO hydrogenation favorable to ethylene rather than methane are very probably located on the most external surface of alumina. They could be generated by dilute basic aqueous solutions or by pseudo-hydrothermal pretreatment.

4. Conclusion

This paper, as a supplement of a previous paper, further demonstrates that coordinatively unsaturated metal and oxygen counterions are very probably active sites for CO hydrogenation favorable to ethylene rather than to methane. The precursors of these active sites may be a very thin layer of boehmite which could be generated by basic aqueous solution and pseudo-hydrothermal pretreatment of alumina.

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