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Cr_2O_3 promoted skeletal Cu catalysts for the reactions of methanol steam reforming and water gas shift

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Abstract

Promotional effects of chromia on the structure and activity of skeletal copper catalysts for methanol steam reforming and water gas shift have been studied. Catalysts were prepared by leaching $CuAl_2$ alloy particles in aqueous NaOH solutions containing sodium chromate at various concentrations. XPS spectra showed that the surface of the resulting catalysts mainly consisted of Cr^{3+} compounds and Cu^0. Cu^+ and/or Cu^{2+} were not observed by XPS.

Increasing the concentration of chromate in the leach liquor resulted in decreases in pore diameter and copper crystallite size but significant enhancement of BET surface area was observed while the total pore volume was maintained. The addition of small amounts of chromate to the leach liquor significantly enhanced the Cu surface area. However, higher concentrations of chromate in the leach liquor decreased the Cu surface areas although the total surface areas increased.

The activities of Cr_2O_3 promoted skeletal copper catalysts for both methanol steam reforming and water gas shift reactions were determined separately. The results indicated that deposition of Cr_2O_3 on skeletal copper catalysts significantly improved the specific activities for these reactions. Chromia is found to act as a structural and catalytic promoter for these reactions.

Keywords: Skeletal copper catalysts; Cr_2O_3 promoted; Methanol steam reforming; Water gas shift

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1. Introduction

Skeletal Cu (also known as Raney® Cu) catalysts have been used in many processes such as low pressure methanol synthesis [1–10], ester hydrogenolysis [11–13], methanol dehydrogenation to methyl formate [14,15], methanol steam reforming and water gas shift reactions [7,9], etc. Early studies of these catalysts [1,3–5] were concerned with the preparation of the catalysts by alkali leaching of copper–zinc–aluminum alloy particles or pellets. The resultant catalysts were a skeletal structure copper with significant zinc oxide contents and low levels of aluminum and were found to be very active for methanol synthesis [1–5]. Evans et al. [11] studied hydrogenolysis of ethyl formate using copper-based catalysts including skeletal Cu as well as Zn and Cr promoted skeletal Cu catalysts. It was observed that Cr promoted skeletal Cu and skeletal Cu itself were more active in ethyl formate hydrogenolysis than Zn promoted skeletal Cu, commercial copper chromite and co-precipitated Cu–ZnO–Al_2O_3 methanol synthesis catalysts. Skeletal Cu catalysts were also found to be the most active and selective catalysts for dehydrogenation of methanol to produce methyl formate [14,15], although the problem of severe deactivation resulting from a formaldehyde-based polymer fouling the copper surface was observed [16].

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Recent attention has been paid to the application of promoted skeletal copper catalysts to the methanol steam reforming and water gas shift reactions [7–9] which are the important reactions in the production of hydrogen for fuel cells [17–23]. Preliminary studies [8,9] have shown that chromia promoted skeletal Cu catalysts, prepared by leaching $CuAl_2$ alloy particles in a 6.1 M NaOH solution containing sodium chromite ($NaCrO_2$), are more active than skeletal Cu for these reactions. However, extensive studies of the effect of chromia loading were limited because of difficulties of increasing sodium chromite concentration in the leach liquids — due to the limitation of $Cr_2O_3{\cdot}xH_2O$ solubility in caustic. An alternative route to add chromia into skeletal Cu catalysts has been suggested in a previous paper [10]. The resultant catalysts have been found to result in better selectivity for methanol synthesis than the original skeletal Cu catalyst [10].

This paper reports the studies of the preparation of chromia promoted skeletal Cu catalysts using the method suggested in [10] and the effect of chromia in skeletal Cu catalysts on the structures, properties of the surface and activities for methanol steam reforming and water gas shift reactions.

2. Experimental

2.1. Catalyst preparation and characterization

The method used to prepare Cr_2O_3 promoted skeletal Cu catalysts was identical to that described in a previous study [10]. Particles (210–350 μm) of $CuAl_2$ alloy (52.17 wt.% Al and 47.83 wt.% Cu) were leached in 6.1 M NaOH solutions containing various concentrations of Na_2CrO_4 from 0 to 0.3 M at 273 K for 72 h. The resultant samples were washed thoroughly using distilled water until neutral pH and stored under distilled water prior to use. The solutions containing Na_2CrO_4 were prepared by adding $Na_2Cr_2O_7$ into a 6.1 M NaOH aqueous solution. For comparative testing, a commercial copper chromite catalyst (Harshaw: Cu-0203T) was used. Two separate batches of skeletal catalysts containing Cr_2O_3 within the range 0–6.5 wt.% were prepared for the characterization and for the activity evaluation.

The leached samples were characterized by determining their chemical states of the surface, surface area, pore structure, Cu crystallite size and composition, etc. The chemical states of the catalyst surface were analyzed by X-ray photoelectron spectroscopy (XPS) (Kratos XSAM800) using a Mg Kα X-ray source operating at 225 W. XPS elemental region spectra were acquired using fixed analyzer transmission (FAT) mode at a pass energy of 20 eV resulting in spectral energy resolution of 0.88 eV (FWHM) for the Ag $3d_{5/2}$ transition. Each sample was wet loaded into the vacuum chamber without exposing to the air and dried carefully under the vacuum overnight until the system pressure was below 1E−9 torr prior to the analysis.

The surface area measurements were carried out in a flow system (Flowsorb [24]). Catalyst samples were wet loaded into the testing tube and dried at 423 K in a hydrogen flow for 30 m and for another 1 h at 523 K in hydrogen, before being flushed and cooled to 363 K in flowing high purity helium. The Cu surface area was determined at 363 K using a N_2O decomposition technique [24], followed by total surface area measurements using a single point BET method (nitrogen adsorption–desorption at 77.5 K). Pore structure and pore size distributions of the samples were obtained from N_2 adsorption–desorption isotherms at 77.5 K using a Micromeritics ASAP 2000 apparatus.

The Cu crystallite sizes were determined by X-ray diffraction (Phillips expert system) using Ni-filtered Cu Kα (wavelength = 1.543 Å) radiation. The sample (covered by distilled water to avoid oxidation of the catalyst) was uniformly spread on the surface of a silica sample holder prior to XRD examination and scanned from 40° to 47° (2θ). The Cu (1 1 1) peak was employed to calculate Cu crystallite size using the Scherrer equation. The contents of Cr in the catalysts were determined by atomic absorption spectroscopy (Varian/Spectr AA-20 plus) on acid-digested samples.

2.2. Catalyst testing

Activities of the catalysts for the reactions of methanol steam reforming (SR) and water gas shift (WGS) were determined using a conventional microreactor flow system. Liquid feedstock was pumped to a stainless steel reactor (6.35 mm OD, 100 mm length) using an ISCO LC-2600 pump attached to an evaporator. Gas flow rates were controlled using Brooks 5850 mass flow controllers. Products were analyzed using a Shimazu 9A gas chromatograph fitted with a thermal conductivity detector after separation using a Porapak Q column (3 m) at 383 K.

An amount of 0.15 ml of catalyst was wet loaded in the constant temperature zone of the reactor and dried in a hydrogen:helium (1:4) mixture at 473 K for 5 h. The feedstock for the water gas shift reaction (CO: 120 ml STP/min, H_2O: 5.8 ml(liq.)/h) was then introduced. A small amount of hydrogen (26 ml STP/min) was added to the feed in order to avoid oxidation of the catalyst by oxygen dissolved in water. The exit gases were passed a cold trap at 273 K to lower the water content and to improve the sensitivity of the gas chromatographic analysis. The catalyst was stabilized under the feeding conditions overnight (about 16 h) before activity measurements were carried out. After testing the activity for the water gas shift reaction, the system was purged with H_2/He (1/4) for 1 h and methanol steam reforming feedstock (methanol:water (mol) 1:1) was introduced at 8 ml(liq.)/h carried in He (80 ml STP/min). The measurements for steam reforming activity started after the system had reached a steady state as indicated by the product analysis.

The WGS activity was reported as moles of CO converted per gram of copper in the catalyst per hour.

The SR activity was defined as moles of CO_2 and CO formed per gram of copper in the catalyst per hour.

3. Results and discussions

3.1. XPS characterization

Two samples were designed for XPS testing. One was pure skeletal Cu prepared by leaching $CuAl_2$ in a 6.1 M NaOH solution at 273 K for 16 h. The other sample was promoted skeletal Cu prepared by leaching $CuAl_2$ in a 6.1 M NaOH solution containing 0.3 M Na_2CrO_4 at 273 K for 72 h.

The XPS survey spectra are shown in Fig. 1 for both skeletal Cu and Cr_2O_3-promoted skeletal Cu. Although small amounts of oxygen were detected from the surface of the skeletal Cu, high resolution spectra of Cu $2p_{3/2}$ and Cu $L_3M_{45}M_{45}$ indicate that the surface basically consisted of metallic Cu. The binding energy (BE) of Cu $2p_{3/2}$ is precisely measured as 932.3 eV. It is noted that this value is 0.4 eV lower than that for the reference of pure copper and seems to be close to the value for Cu^+ [25]. However, the kinetic energy (KE) of Cu $L_3M_{45}M_{45}$ is 918.7 eV, clearly

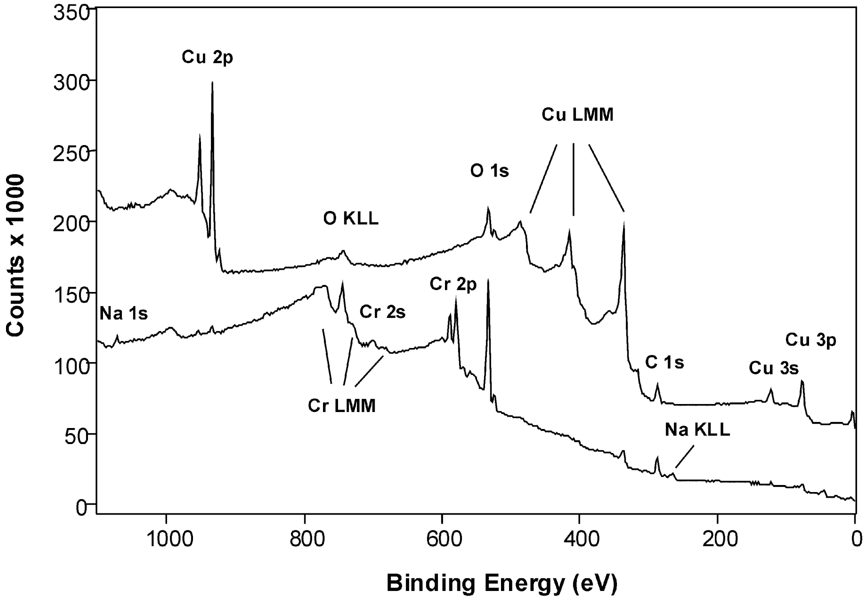

Fig. 1. Wide scan XPS spectra for both skeletal Cu (a) and Cr_2O_3-promoted skeletal Cu sample (b). The catalyst was prepared by leaching $CuAl_2$ alloy particles (a) in a 6.1 M NaOH at 273 K for 16 h and (b) in a 6.1 M NaOH solution containing 0.3 M Na_2CrO_4 at 273 K for 72 h.

indicating that the copper is in the Cu^0 state [25]. If the surface were mainly Cu_2O, the KE of $L_3M_{45}M_{45}$ would be about 2 eV lower. The modified Auger parameter (AP), defined as $BE(Cu\,2p_{3/2}) + KE(Cu\,L_3M_{45}M_{45})$, for this sample is 1851.0 eV, also indicating the Cu^0 state. On other hand, as little shake-up feature was observed in the Cu 2p spectrum (Fig. 2), it is most likely that Cu^{2+} is not present.

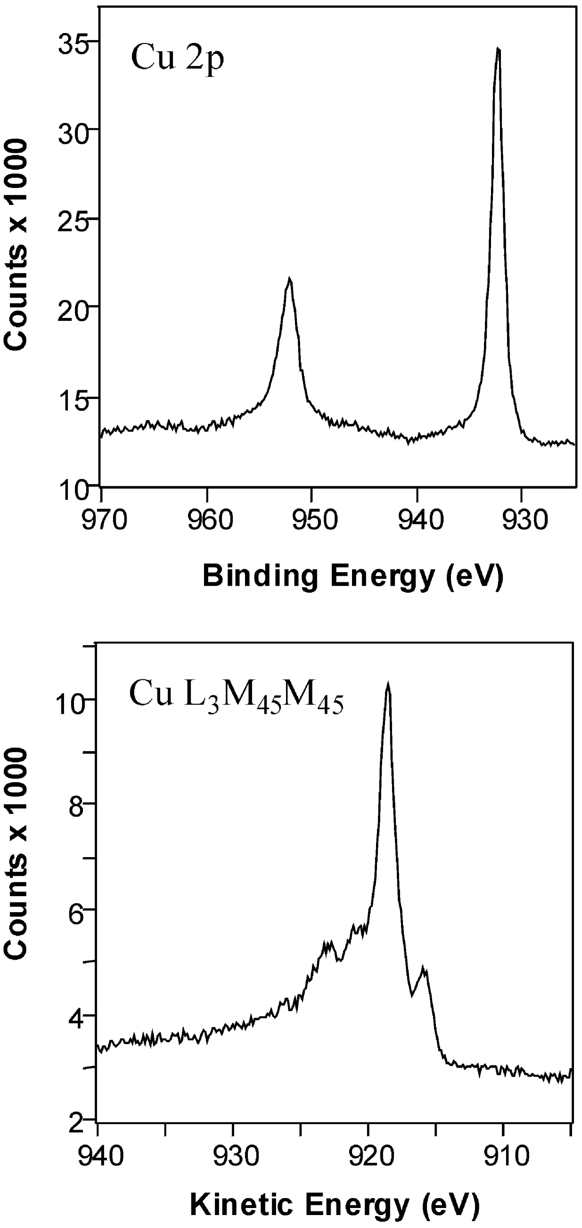

Fig. 2. Narrow scan spectra of Cu 2p and Cu LMM for skeletal Cu sample.

For the Cr_2O_3-promoted skeletal Cu sample, a very intense signal for chromium is observed. The atomic ratio of Cr–Cu on the surface of the sample is as high as 11.5. Considering that bulk chemical analysis indicated only 6.45% of chromium-compound (expressed as Cr_2O_3) in the catalyst, the surface analysis reveals that most of chromium compounds are present at the surface of the copper skeleton. The measured binding energy of Cr $2p_{3/2}$ (Fig. 3) is 557.1 eV, indicating Cr^{3+} status, existing as Cr_2O_3 and/or $Cr(OH)_3$ [25] which decomposes when heated to form Cr_2O_3 [26]. Although the intensities of the copper signals in this sample are largely reduced in comparison to the unpromoted skeletal Cu sample, peak positions of both Cu $2p_{3/2}$ and Cu $L_3M_{45}M_{45}$ were identical. This suggests that the copper still remains as Cu^0 although Cr^{3+} compounds are presented on the surface.

The XPS results clearly show that Cr^{3+} compounds are present on the surface of the promoted skeletal Cu catalyst, indicating that Cr^{6+} in chromate in the leach liquor was reduced into Cr^{3+} which may exist as Cr_2O_3 or $Cr(OH)_3$. The skeletal Cu remains as Cu^0. No Cu^+ and Cu^{2+} were observed, suggesting that Cr^{6+} was reduced by oxidation of Al not Cu.

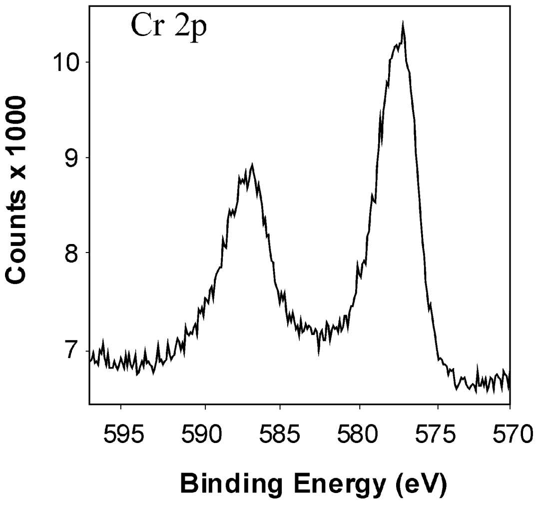

Fig. 3. Narrow scan XPS spectrum of Cr 2p for promoted skeletal Cu sample.

Table 1
Effect of Na_2CrO_4 concentration on structure and surface area of skeletal Cu catalysts

Na_2CrO_4 in the caustic (M)	Cr_2O_3 content (wt.%)	Average pore diameter (nm)	Total pore volume ($cm^3\,g^{-1}$)	BET surface area ($m^2\,g^{-1}$)	Cu surface area ($m^2\,g^{-1}$)	S_{Cu}/S_{BET}	Cu crystallite size (nm)
0	0	32.4	0.16	19.5	8.2	0.42	14.7
0.001	0.49	25.8	0.18	30.3	14.3	0.47	12.9
0.002	0.75	21.2	0.17	32.2	14.9	0.46	11.7
0.004	1.36	16.4	0.17	42.2	18.0	0.43	10.7
0.008	3.39	11.9	0.17	54.7	17.0	0.31	10.4
0.0146	4.36	9.5	0.16	63.6	14.4	0.23	10.1
0.3	6.45	8.7	0.14	64.1	11.1	0.17	9.5
Cu-0203T	20	22.3	0.04	11.8	6.2	0.53	–

3.2. Effect of sodium chromate in the leach liquor on structure and surface of skeletal Cu catalysts

It is clear that the presence of sodium chromate in the leach liquor led to deposition of Cr_2O_3 on the surface of skeletal Cu. Effects of the concentrations of sodium chromate on structure and surface area of the resultant catalysts were examined. The results are shown in Table 1 and Fig. 4. The results in Table 1 show that by increasing the concentration of chromate in the leach liquor, the pore diameter and copper crystallite size decreased and BET surface area correspondingly increased while the total pore volume was maintained essentially constant.

At least one reason for the increased surface area became clear from pore size analysis (Fig. 4). It is seen that the presence of Na_2CrO_4 in the leach liquor resulted in narrowing the pore distribution and reducing the average pore size but the total pore volume was maintained. This means that the number of pores in the catalyst has been increased. It is the increased number of pores that accounts for the observed increase in BET surface area.

The addition of small amounts of chromate to the leach liquor significantly enhanced the Cu surface area and BET surface area of skeletal Cu, for chromate concentrations of 0.001 and 0.004 M. The results (Table 1) also show that higher concentrations of chromate in the leach liquor caused significant decreases to the

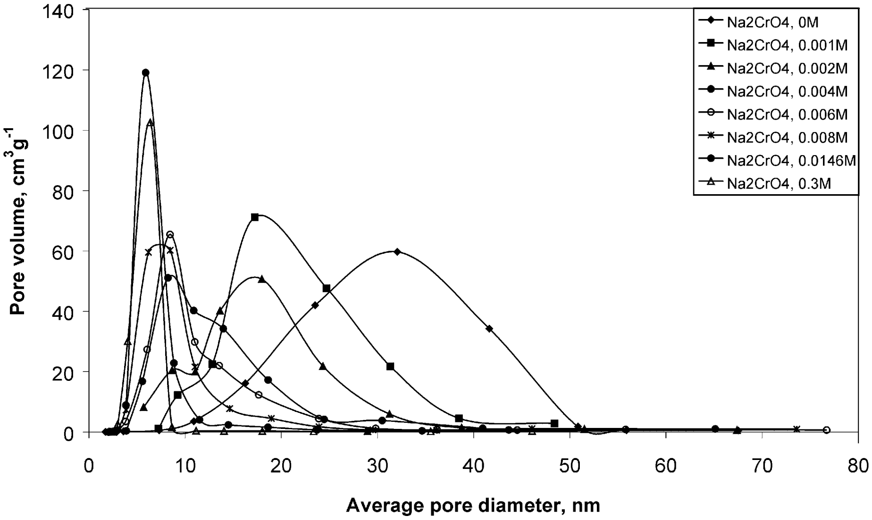

Fig. 4. Effect of sodium chromate in the leach liquor on pore size distribution of the catalysts.

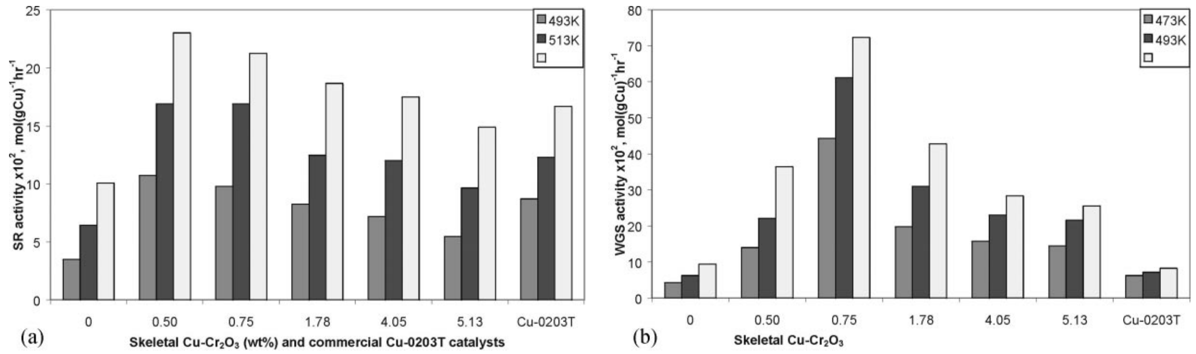

Fig. 5. Comparison of the activities of promoted skeletal copper catalysts with a commercial copper chromite (Cu-0203T) catalyst for methanol steam reforming (a) and water gas shift (b) reactions.

ratio of Cu surface area to BET surface area although the total surface areas increased. This is not surprising because higher concentrations of chromate result in depositing larger amounts of Cr_2O_3 on the surface of skeletal Cu (Fig. 1) thereby decreasing the Cu surface area. It is obvious that the presence of chromate in the leach liquor results in significant improvement of the BET surface area due to promotion of the overall structure of the catalyst. However, larger amounts of Cr_2O_3 deposited on the surface result in a decrease in the Cu surface area due to blocking of surface sites.

3.3. Effect of Cr_2O_3 in skeletal Cu catalysts on activities of methanol steam reforming and water gas shift reactions

Activities of the Cr_2O_3-promoted skeletal Cu catalysts for the reactions of methanol steam reforming and water gas shift are plotted in Fig. 5a and b. Comparisons with a commercial copper chromite catalyst (Harshaw Cu-0203T: CuO 80%, Cr_2O_3 20%) are also made in this figure. The effect of Cr_2O_3 in the skeletal Cu catalysts on activities of methanol steam reforming and water gas shift is shown in Fig. 6a and b.

The results in Figs. 5 and 6 clearly show that small amounts of Cr_2O_3 in skeletal Cu catalysts significantly improved the specific activities for both methanol steam reforming and water gas shift reactions. The turnover frequency data indicate that Cr_2O_3 acts as a promoter to improve the catalytic activity of copper for these reactions. However, larger amounts of Cr_2O_3 in the skeletal Cu catalysts decreased the specific activity, although Cr_2O_3 itself has some catalytic activity for these reactions [9].

It is also seen from Fig. 5 that the optimal concentration of Cr_2O_3 in skeletal Cu catalysts for the reaction

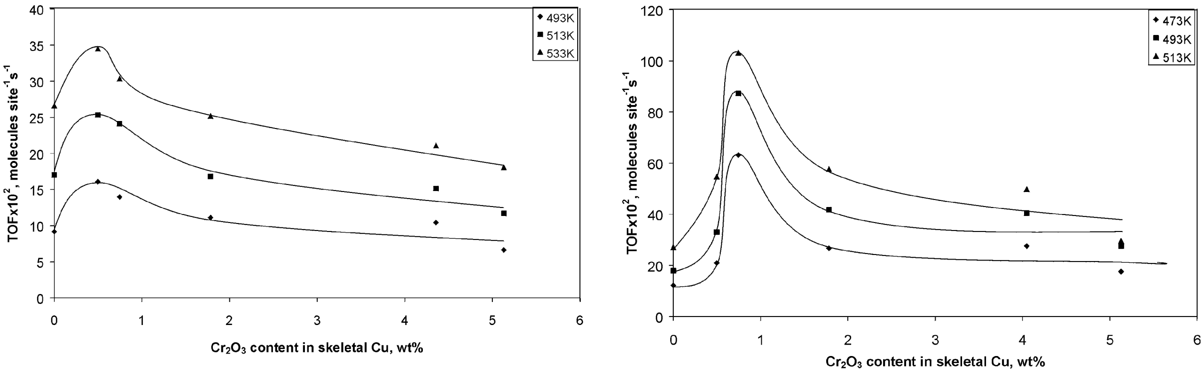

Fig. 6. Effect of Cr_2O_3 content in skeletal Cu catalyst on activities of methanol steam reforming (a) and water gas shift (b) reactions — expressed as turnover frequencies.

of methanol steam reforming is 0.5%. At this point, the SR activity at 513 K is 2.3 times of that of the unpromoted skeletal Cu catalysts and is almost 38% higher than that of the commercial Cu-0203T catalyst. For the water gas shift reaction, 0.75 wt.% Cr_2O_3 in the skeletal Cu catalyst achieved the best performance for the reaction. The WGS activity of this catalyst is 8–10 times of that of the original skeletal Cu catalyst and is more than seven times of that of Cu-0203T catalyst.

4. Conclusions

The relative importance of chromium oxide as a structural and catalytic promoter of skeletal copper catalysts has been examined. The promoter was added to the catalysts by leaching $CuAl_2$ in 6.1 M sodium hydroxide solutions containing sodium chromate. Deposition of Cr^{3+} compounds on the skeletal Cu was identified by the XPS technique.

Increasing the concentration of chromate in the leach liquor led to increased Cr_2O_3 loadings and decreased pore diameters and copper crystallite sizes and large increases in BET surface area due to the increased number of pores in the catalyst.

Small amounts of Cr_2O_3 in skeletal copper catalysts significantly promoted the activities for methanol steam reforming and water gas shift reactions. The effects of Cr_2O_3 contents on activities of skeletal copper were determined. 0.5 and 0.75 wt.% Cr_2O_3 on the surface of skeletal copper produced highest activity for methanol steam reforming and water gas shift, respectively. These particular catalysts have much higher activities than a commercial copper chromite catalyst which was used for comparative testing.

Acknowledgements

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