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Catalytic decomposition of methane on Raney-type catalysts

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ABSTRACT

The catalytic decomposition of methane into CO_x-free hydrogen and filamentous carbon was investigated on Raney-type catalysts. Catalysts performance was assessed by comparing the measured conversions with the equilibrium values and with selected results reported recently. The activity, selectivity and stability were dependent on the alloy composition and preparation method (conventional or quenched alloy types), as well as the operating conditions. Textural properties, chemical compositions and catalyst performances were determined, and the carbon deposits were characterized by different techniques. Ni and Co catalysts obtained from Raney-type alloys prepared by quenching showed better performance for methane decomposition than conventional systems, with conversions approaching equilibrium. The stability of the catalysts could be extended by increasing the contact time and by hydrogen pre-treatment of the catalysts. The carbon deposits consist mostly of carbon nanofibres and carbon nanotubes. In addition to the high activity and stability for methane decomposition, there was no generation of carbon oxides, which makes these catalysts suitable for the production of pure hydrogen for fuel cells.

1. Introduction

Concerns over the environment and depletion of fossil fuels led to the concepts of "hydrogen-energy system" and "hydrogen economy". Hydrogen is a convenient energy carrier which can be used efficiently and without any emissions in fuel cells. Hydrogen is mostly produced by steam reforming of methane, which also yields CO and CO_2. For fuel cell applications, however, very low levels of carbon oxides are tolerated. An interesting alternative process is the catalytic decomposition of methane ($CH_4 \rightleftharpoons C + 2H_2$), especially if the carbon by-product can be obtained in suitable form for practical applications, such as carbon nanofibres or nanotubes [1]. Thus, there has been an intense research effort on this topic in recent years. Various types of carbon materials (activated carbons, carbon blacks) have been used as catalysts for this purpose [2–6]. However, in general, carbon materials perform rather poorly, since the methane conversions reported are quite low, and there is strong deactivation due to carbon deposition. It also became clear that the carbon deposits are not catalytically active themselves for further methane decomposition [4].

Metal catalysts for this reaction are usually based on Ni, Co or Fe [7–27], which is not surprising, since these are well known active catalysts for hydrocarbon decomposition and carbon formation [28,29]. Supported catalysts such as Ni/Al_2O_3 have moderate activities, but generally they are not very stable. The best results have been obtained with high metal loaded catalyst systems [7,16]. Therefore, massive catalysts seem to be a good choice for the proposed task.

In the present work we report promising results obtained with massive skeletal catalysts (Raney-type Ni, Co and Fe). The effect of the operating conditions on the activity, selectivity and stability of these catalytic systems, and on the type of carbon formed, was investigated in detail. To our knowledge there is only one very recent report on this type of catalyst for methane decomposition, where the emphasis was on carbon nanofibre formation [30].

2. Experimental

2.1. Catalysts

The skeletal (Raney-type) catalysts used in this work were prepared from Me–Al alloys (Me = Ni, Co or Fe) obtained from two different sources. The nominal active metal mass content in the alloys are 50 and 30 wt% for Ni, 50 and 30 wt% for Co, 50 and 35 wt% for Fe. The Ni 50 wt% alloy is a commercial product from Fluka Chemie Gmbh. The remaining alloys used were supplied by H.C. Starck GmbH (Amperkat® SK alloys). The Ni30, Co30 and Fe35 alloys are obtained by a fast quenching method [31], and the remaining alloys are conventional products [32].

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Prior to the reaction tests, the Raney-type alloys were activated by leaching out the aluminium with a concentrated NaOH solution at room temperature for 2 h [33]. The catalysts were subsequently washed several times with distilled water and kept in a flask with ethanol as required by their pyrophoric nature. In this work, the catalysts are designated by the original composition of the alloys. Thus, catalyst Ni30 is the catalyst obtained by leaching out the Al from the 30%Ni–70%Al alloy.

2.2. Reaction studies

Temperature programmed reaction (TPRe) experiments were carried out with a custom built setup, consisting of a U-shaped tubular micro-reactor, placed inside an electrical furnace. The flow rate of methane (2.5 N cm^3/min) diluted in helium carrier gas (25 N cm^3/min) and a temperature program from room temperature to 800 °C at a heating rate of 5 °C/min was controlled with appropriate equipment. The amounts of H_2 ($m/z = 2$), CH_4 ($m/z = 16$), C_2H_2 ($m/z = 26$), CO or C_2H_4 ($m/z = 28$), NO or C_2H_6 ($m/z = 30$), and CO_2 ($m/z = 44$) were monitored with a quadrupole mass spectrometer.

For the isothermal reaction studies, the catalysts were loaded into a tubular reactor, and dried overnight at 78 °C in a nitrogen stream of 100 N cm^3/min. In some cases, the catalysts were pre-treated in hydrogen for 2 h at 600 °C with a total gas flow rate of 110 N cm^3/min and a composition corresponding to a H_2/N_2 molar ratio of 1:10. This treatment is hereafter referred to as HPT.

The continuous-flow reactor was a 75 cm long silica tube with 2.7 cm i.d., inserted into a furnace with a PID temperature controller. The flow rates of methane (99.999%), nitrogen (99.995%) and hydrogen (99.999%) were controlled by mass flow controllers. In most of the experimental runs the feed composition was a gas mixture of methane and nitrogen (molar ratio of 1:10) with a total gas flow rate of 110 N cm^3/min. During the reaction, the composition of the outgoing gas stream was determined with a gas chromatograph equipped with a capillary column (Carboxen 1010 Plot, Supelco) and a thermal conductivity detector.

2.3. Characterization of catalysts and carbon deposits

The particle size distributions of the alloys and the corresponding catalysts were measured with a laser particle size analyzer Coulter LS 230.

The specific surface areas of the fresh catalysts were calculated by the BET method from the N_2 equilibrium adsorption isotherms at 77 K, determined with a Coulter Omnisorp 100 CX apparatus.

The alloys, catalysts and carbon deposits were examined with a JEOL JCM-35C scanning electron microscope (SEM) associated with an energy dispersive X-ray analyzer (EDX) Tracor TN-2000.

A high-resolution transmission electron microscopy (TEM) study of the carbon deposits was carried out with a Phillips CM12 instrument.

X-ray photoelectron spectra (XPS) of the alloys and catalysts were acquired in a VG Scientific Escalab 200A apparatus. Quantitative results were obtained by fitting the experimental peaks to Gaussian–Lorentzian curves, measuring the spectral areas corresponding to each chemical element of interest and applying their respective empirical sensitivity factors.

3. Results

3.1. Catalysts characterization

The properties of the Raney-type alloys and their corresponding catalysts are collected in Table 1. It is observed that the particle sizes of the Ni50, Ni30, Co30 and Fe50 catalysts are approximately half of those of the original alloys, while Co50 and Fe35 kept approximately their original size. The BET surface areas of the catalysts are within the range of reported values for this type of catalysts [34]. It is also observed that the catalysts Ni30, Co30 and Fe35 exhibit lower surface areas and higher particle sizes than Ni50, Co50 and Fe50, respectively, most probably as a result of the different preparation methods of the original alloys. For the alloys, the atomic ratios $R^{a}_{\mathrm{eff,alloy}} = (\text{active metal}/\text{total metal})$ determined by EDX are in good agreement with the nominal values $R^{a}_{\mathrm{n,alloy}}$. Upon activation, the corresponding atomic ratios in the catalysts $R^{a}_{\mathrm{eff,catalyst}}$ are much higher, due to the removal of most of the Al. The residual Al left is present as Al_2O_3, as confirmed by EDX. It should be noticed that the residual amount of Al is higher in the Ni50 catalyst, all other catalysts being richer in the active metal. The residual alumina left after leaching will act as a structural promoter, stabilizing the catalyst structure against sintering, in a similar way as for other massive catalysts reported in the literature [14,24,35]. The residual quantity of Al in Raney-type Ni catalysts depends on the original alloy [36]. Various phases may be present, such as $NiAl_3$, Ni_2Al_3 and NiAl. The higher the content of Ni in these intermetallic phases, the lower is their reactivity towards leaching by NaOH. The Ni50 and Ni30 alloys have different amounts of these phases. For instance, the Ni50 alloy contains both Ni_2Al_3 and $NiAl_3$, while Ni30 contains mostly $NiAl_3$. Therefore, the residual amount of Al in the Ni50 catalyst is larger, due to the lower leaching rate of the Ni_2Al_3 phase relatively to $NiAl_3$ [37,38].

Table 1
Characterization of the Raney-type alloys and corresponding catalysts

Sample	Alloy			Catalyst		
	$\bar{d}$ (μm)	$R^{a}_{\mathrm{n,alloy}}$	$R^{a}_{\mathrm{eff,alloy}}$	$\bar{d}$ (μm)	$R^{a}_{\mathrm{eff,catalyst}}$	S_{BET} (m^2/g)
Ni50	36	0.315	0.39 ± 0.06	21	0.72 ± 0.07	82
Ni30	285	0.165	0.17 ± 0.02	156	0.85 ± 0.07	64
Co50	62	0.314	0.30 ± 0.05	59	0.85 ± 0.16	41
Co30	372	0.164	0.17 ± 0.02	211	0.94 ± 0.06	26
Fe50	86	0.326	0.35 ± 0.09	43	0.95 ± 0.05	62
Fe35	51	0.206	0.23 ± 0.06	63	0.95 ± 0.19	24

$\bar{d}$: average particle size of the powders; $R^{a}_{\mathrm{n,alloy}}$: nominal atomic ratio active metal/total metals; $R^{a}_{\mathrm{eff,alloy}}$: determined effective atomic ratio active metal/alloy metals; $R^{a}_{\mathrm{eff,catalyst}}$: determined effective atomic ratio active metal/catalyst metals; S_{BET}: specific surface area.

Fig. 1a–c shows SEM micrographs of the catalysts Ni50 (Fig. 1a), Ni50 pre-treated in hydrogen (Fig. 1b) and Ni30 (Fig. 1c). Comparison of these micrographs shows that the microstructure of Ni50 becomes similar to that of Ni30 upon hydrogen treatment (HPT). Catalysts Co50, Fe50 and Fe35 show nearly the same morphology as Ni50, and the catalyst Co30 is similar to Ni30. The Co50, Fe50 and Fe35 catalysts pre-treated with hydrogen show morphologies similar to Ni30 (or Co30). The more fragmented microstructure of Ni30 and Co30 is typical of alloys which have been quenched rapidly during the production process, and this microstructure is kept also after leaching with an alkaline solution [31].

Table 2 shows the surface characterization of the Me–Al alloys and the corresponding catalysts, obtained by XPS. In the case of the alloys, the results show that the particles are mostly covered with an Al_2O_3 layer. The higher the Al content in the original alloy, the higher is the amount of Al_2O_3 found on the surface [38,39].

Upon activation, the XPS spectra of the catalysts show that Ni and Co are mostly in the zero-valent state, confirming that there is no formation of oxides or hydroxides when the corresponding alloys are attacked by NaOH, in agreement with the literature [33,39–41]. Thus, any oxygen remaining in the catalyst must be bound to Al, or is present as adsorbed species. The presence of residual Al or alumina was detected and also reported by other