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Microcalorimetric studies and methane reforming by CO_2 on Ni-based zeolite catalysts

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Abstract

A series of catalysts containing nickel, based on HZSM-5 and USY zeolites, have been prepared by ionic exchange; a Ni/γ-Al_2O_3 catalyst has been prepared by impregnation, for comparison. Ammonia and CO adsorption microcalorimetry and temperature programmed reduction experiments have shown that NiZSM-5 is the most acidic and the most reducible catalyst. The study of the reaction of methane reforming by carbon dioxide in presence of these catalysts has shown that the catalytic performance depends simultaneously on the acidity, reducibility, and structure of the zeolite. Globally, it appears that the catalytic properties of NiUSY are superior to those of NiZSM-5 and Ni/γ-Al_2O_3.

1. Introduction

The use of heterogeneous catalysts in the industry is determined by their activities in a number of particular chemical reactions. Elucidating the origin of catalytic activity on a molecular level requires understanding the nature, number, strength, and distribution of specific active sites on the surface [1–3]. A correlation between the catalytic activity and the characteristics of the active sites has been established for a variety of chemical reactions. Therefore, many physical and chemical methods have been developed and applied to evaluate the properties of active sites, based on the adsorption of some typical probe molecules and their interaction with the catalyst surface [4–6]. Thermal methods such as temperature programmed desorption (TPD) [7–10] and adsorption calorimetry [5,6,11,12] of probe molecules give information regarding the strength and distribution of active sites.

In addition, the catalytic properties of zeolites are closely related to their ability to adsorb a variety of molecular species into the structure; this possibility is in turn influenced by the nature of the charge-balancing cations [13–16]. Therefore, CO as a probe molecule has attracted a great deal of attention because many catalytic reactions involve CO directly [17].

Accordingly, we have used microcalorimetric measurements of the heats of ammonia and carbon monoxide adsorption on NiUSY and NiZSM-5 zeolites, and for comparison on a Ni/γ-Al_2O_3 sample, in order to describe the quantitative energetic features of surface sites.

2. Experimental

2.1. Catalysts

The samples used in this study were prepared from synthetic dealuminated USY faujasite and HZSM-5 type zeolites provided, respectively, by Union Carbide and Degussa. The Ni^{2+} exchanged samples were obtained by conventional ion-exchange procedure [18], while the Ni/γ-Al_2O_3 catalyst was prepared by classical impregnation with $Ni(NO_3)_2$ solution. The resulting solids have been dried at 110 °C and calcined at 500 °C. The samples are listed in Table 1.

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Table 1
Chemical composition of the catalysts

Catalysts	Ni (wt%)	Si/Al	Exchange level (%)	S_{BET} (m^2/g)
NiUSY	8.7	3.5	81	514
NiZSM-5	3.5	14.0	106	330
Ni/γ-Al_2O_3	8.1	–	–	150

2.2. Characterization

The chemical composition of the catalysts has been determined by ICP flame spectroscopy. The specific surface areas have been determined by the BET method using a Coultronics apparatus. The results are summarized in Table 1.

The radiocrystallographic analysis of the samples has been performed in a Philips PW1050/81 automated powder goniometer (λ Cu(Kα) = 1.54184 Å). XRD patterns were recorded for all samples in order to evaluate possible changes in the crystallinity of the zeolites (Fig. 1A–C). It appears that the crystallinity of the zeolites decreased only slightly upon Ni incorporation and calcination, in agreement with the results reported by Kiessling et al. [19].

The differential heats of NH_3 and CO adsorption (expressed in kJ per mole of gas adsorbed) have been determined in isothermal conditions in a heat flow calorimeter of Calvet type (SETARAM C80) coupled to a volumetric apparatus. During adsorption, the pressure variations were recorded using a thermostatic Barocel membrane manometer [20,21]. The samples were pretreated under vacuum at 400 °C prior to adsorption. The adsorption of successive doses of NH_3 or CO was performed at 150 or 30 °C, respectively, until an equilibrium pressure of 66 Pa was reached. The calorimetric and volumetric data were used to plot the differential heats of adsorption as a function of coverage, and the corresponding adsorption isotherms.

Temperature-programmed reduction (TPR) experiments were carried out in a conventional apparatus equipped with a thermal conductivity detector. About 100 mg of catalyst were loaded in a TPR reactor and pretreated under an argon flow for 90 min at a temperature of 400 °C. The samples were then reduced in an H_2 (1%)/Ar mixture at increasing temperatures up to 700 °C (θ = 3 °C/min).

2.3. Catalytic testing

For reaction tests, usually 100 mg of catalyst were pretreated under helium at 450 °C for 2 h in a tubular "U"-shaped quartz reactor [22]. The reaction temperature was monitored by a thermocouple placed close to the reactor wall, and increased from room temperature to 650 °C at a heating rate

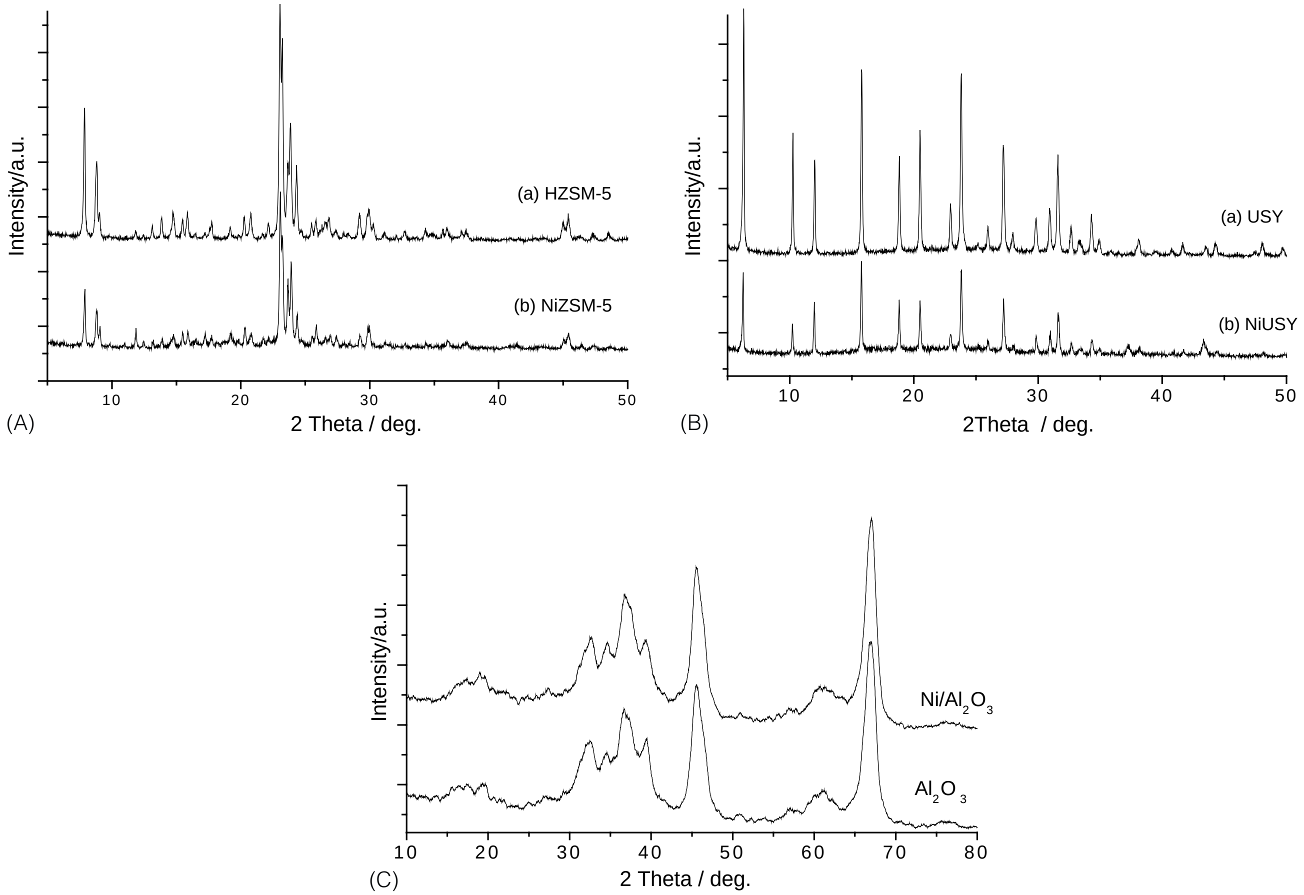

Fig. 1. XRD spectra of: (A) NiZSM-5 and the parent zeolite; (B) NiUSY and the parent zeolite; (C) Ni/γ-Al_2O_3 sample and the parent oxide.

of 4 °C/min. The reactant feed was regulated by mass flow controllers (Brooks 5850 TR). A reaction mixture containing CH_4 and CO_2 in proportion 1:1 was used for the reaction tests, at a flow rate of 20 ml/min. This mixture was allowed to pass trough the sample by switching a four-way valve located at the reactor inlet. Reactants and products were analyzed in an on-line gas chromatograph (Delsi) equipped with a thermal conductivity detector (TCD) and a Carbosieve-B column using helium as carrier gas, and an automatic sampler.

3. Results and discussion

3.1. NH_3 adsorption microcalorimetry

The aim of this work was to find out if there was a relation between the acid–base properties of zeolites, their physicochemical characteristics, and their catalytic activity. The acid–base properties of zeolites depend essentially on the Si/Al ratio and on the presence and nature of any extra-framework species. NH_3 adsorption calorimetry makes it possible to titrate the acid sites and gives information about the acid strength and its distribution. The differential heats of ammonia adsorption for each parent zeolite and the corresponding nickel exchanged catalyst are shown in Fig. 2A and B. The differential heats of adsorption decrease with increasing coverage, tending to a value of about 70 kJ/mol, which corresponds to the limit between physisorption and chemisorption of ammonia at the experiment temperature [4].

When comparing the heats of adsorption of ammonia, the NiUSY and USY samples both display a plateau, around 140 kJ/mol for USY and around 115 kJ/mol for NiUSY. However, the two curves follow a similar trend at low coverage (NH_3 volume < 300 μmol/g), indicating that the introduction of nickel in the USY lattice did not affect much the strong acidity (Fig. 2A). At higher coverages (300 μmol/g < NH_3 volume < 1000 μmol/g), the curve of differential heats for NiUSY lies slightly below the curve for USY. The corresponding isotherms of adsorption are shown in Fig. 3A, confirming these results.

Comparing the HZSM-5 parent zeolite and the corresponding NiZSM-5 sample, Fig. 2B indicates that the NiZSM-5 sample displays a lower plateau of NH_3 adsorption heats (around 125 kJ/mol) than the HZSM-5 zeolite (around 142 kJ/mol). Interestingly, the differential heat curve for HZSM-5 displays an inflection point around 700 μmol/g, while the NiZSM-5 sample shows a continuously decreasing curve, with a much larger total amount of NH_3 adsorbed. These results are confirmed by the corresponding volumetric isotherms (Fig. 3B), and suggest the possibility of the formation of some tetra-amino complexes $[Ni(NH_3)_4]^{2+}$, where the NH_3 molecules are acting as ligands to Ni (II).

The same trend was observed on Ni/γ-Al_2O_3 catalysts and γ-Al_2O_3 support, as reported by Gervasini et al. [23]. A plateau of heats of ammonia adsorption has been observed at 150 kJ/mol on Ni/γ-Al_2O_3 and 155 kJ/mol on γ-Al_2O_3, and a large amount of NH_3 was adsorbed over the Ni/γ-Al_2O_3 sample, also suggesting the formation of ammonia complexes.

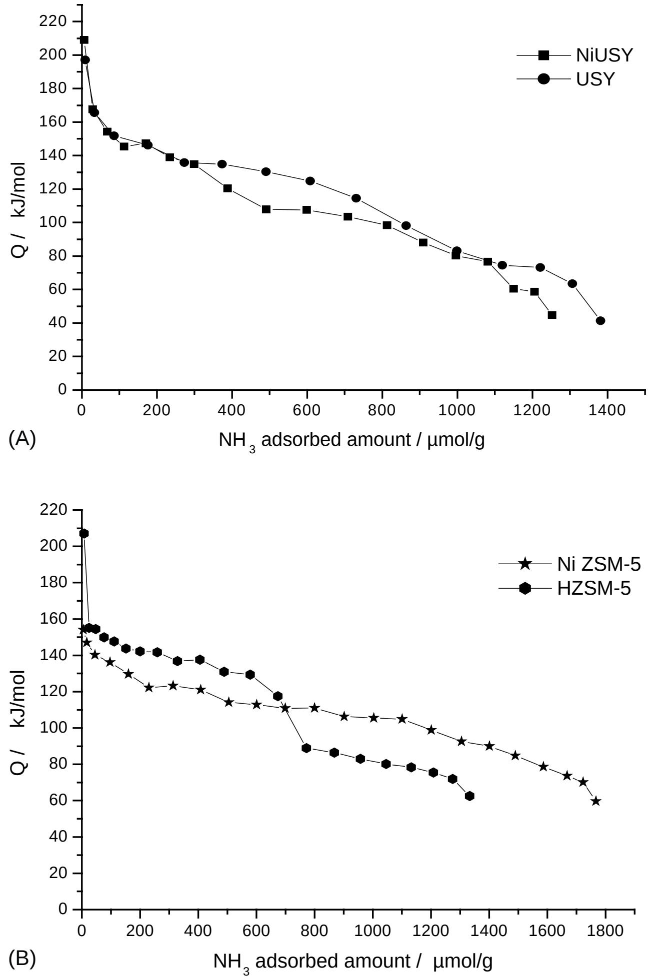

Fig. 2. Differential heats of NH_3 adsorption vs. coverage on: (A) USY and the corresponding nickel exchanged catalyst; (B) HZSM-5 and the corresponding nickel exchanged catalyst.

Both Brönsted and Lewis acid sites are present in zeolites. Brönsted acidity is due primarily to acidic hydroxyl groups attached to the framework, while Lewis acidity is attributed mostly to non-framework aluminium species [24,25]. This is in particular the case for our NiUSY catalyst, where the number of acidic hydroxyl groups attached to the framework is lower than the number of aluminium atoms (the lattice Si/Al ratio as determined by ^{28}Si and ^{27}Al MAS NMR is around 4.5, while the Si/Al ratio measured by chemical analysis is 3.5). On the contrary, the NiZSM-5 sample did not exhibit any extra-framework aluminium species.

3.2. CO adsorption microcalorimetry

Carbon monoxide adsorption is a widely used method for the analysis of active sites on ion-exchanged zeolites. CO as a probe molecule attracts great interest for two main reasons.

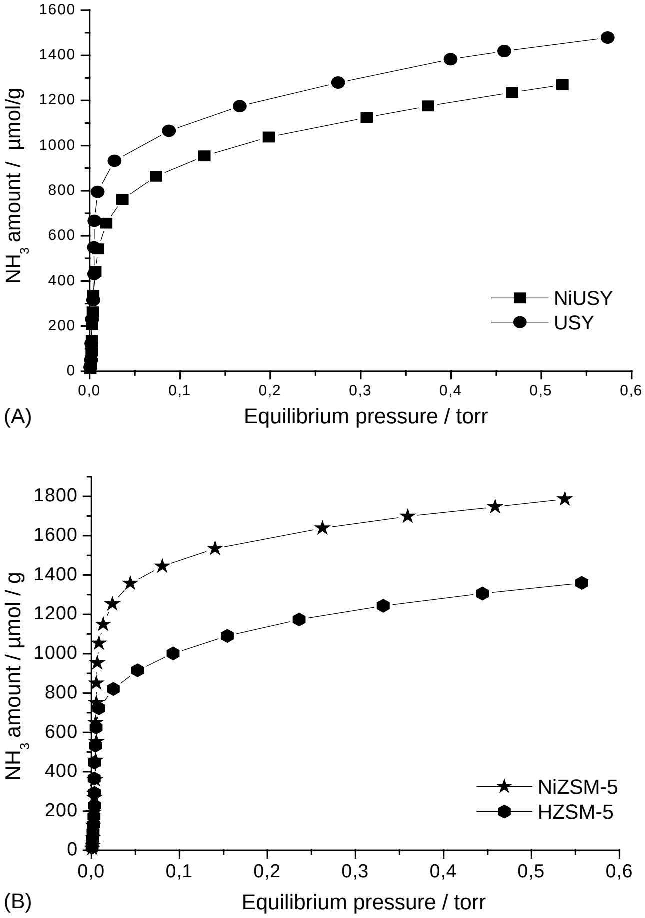

Fig. 3. NH_3 adsorption isotherms on: (A) USY and the corresponding nickel exchanged zeolite; (B) HZSM-5 and the corresponding nickel exchanged zeolite.

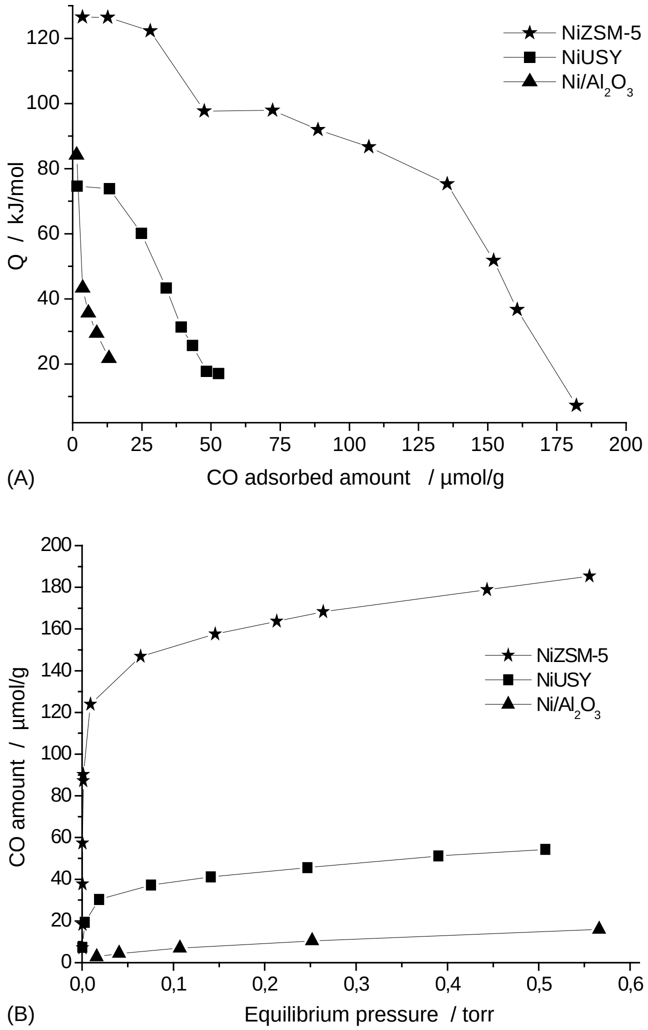

Fig. 4. CO adsorption on Ni-based catalysts: (A) differential heats versus coverage; (B) adsorption isotherms.

First, many catalytic reactions involving CO directly or as an intermediate proceed on metal based catalysts. Secondly, as a result of its ability to act as a weak σ-donor and as a π-acceptor, CO is sensitive to the strong electrostatic fields [26,27] surrounding transition metal cations in zeolite structures. Thus CO meets the requirements defined by Dumesic and coworkers [12] and Zecchina et al. [28] for use as a probe molecule in microcalorimetric measurements at low temperature.

In this work the adsorption of CO was studied in order to elucidate the nature and the strength of active sites in the investigated samples. It was demonstrated that at 25 °C, carbon monoxide interacts with charge balancing cations. Being coordinatively unsaturated, these cations act as a source of Lewis acidity [29].

After the activation process, carbon monoxide was adsorbed on the Ni ion-exchanged zeolites and Ni/γ-Al_2O_3. Fig. 4A presents the values of differential heats of adsorption of CO on the nickel catalysts. The initial heats of adsorption obtained in the case of the NiZSM-5 catalyst (about 127 kJ/mol) are much higher than in the case of NiUSY (about 85 kJ/mol) and Ni/γ-Al_2O_3 (much lower). Two hypotheses can be proposed to explain this difference. First, in most studies of CO adsorption on various zeolites, a non-dissociative adsorption is reported; however, CO decomposition and CO_2 formation have been observed during the adsorption of CO on H^+, K^+, Li^+, Mg^{2+} and Ca^{2+}-exchanged NaX [30]. Thus, the possibility of CO decomposition on active catalytic sites in zeolite systems should be considered [31].

Secondly, it was shown in the literature, based on FT-IR results [32], that for the same charge balancing cation, the polarization of the CO molecule is higher in the case of adsorption on zeolites with higher Si/Al ratios. This could also explain the higher value of the initial heat of CO adsorption in the case of NiZSM-5 (lattice Si/Al = 14.0, since there is no extra-framework Al in this case), compared to that determined for NiUSY (lattice Si/Al = 4.5).

It can also be observed in Fig. 4A that the differential heat of CO adsorption on NiZSM-5 decreases slowly with the amount of CO adsorbed, thus displaying a plateau which suggests the existence of a large number of active sites of similar strength in the structure. On the contrary, in the cases of NiUSY and Ni/γ-Al_2O_3 a sharp decrease of the differential heat of adsorption versus coverage was observed. These results clearly show the existence of a small number of strong active sites for the chemisorption of CO on NiUSY and Ni/γ-Al_2O_3. Fig. 4B confirms these results and indicates that the Lewis site concentrations of the various samples differ according to the following sequence: NiZSM-5 > NiUSY > Ni/γ-Al_2O_3.

3.3. Temperature-programmed reduction

Temperature-programmed reduction experiments were carried out in order to determine the differences in the reducibility of these catalysts, which are related to the location and dispersion of nickel after the calcination step [33,34].

The TPR profiles of the Ni catalysts are collected in Fig. 5. As can be seen, the Ni/γ-Al_2O_3 catalyst displays only one large TPR peak at about 500 °C. It is well known that nickel species on the alumina support mainly exist in the form of $NiAl_2O_4$, which is not readily reducible [35–37].

The reduction of Ni-exchanged zeolites is more complex than for zeolites exchanged by other 3d or 4d elements [38]. It is believed that at low nickel contents a redox equilibrium takes place over zeolite (Z) media, according to the equation:

$$(2Z\text{–}O)Ni^{2+} + H_2 \Leftrightarrow 2Z(OH) + Ni^0.$$

The TPR profile of the NiUSY catalyst displays two large peaks at about 475 and 535 °C. By similarity with the profiles reported in the literature for low content Ni^{2+} exchanged zeolites [39], the observed peaks may be attributed to the reduction of Ni^{2+} ions in different positions: in the supercages (SII sites), and in sodalite cages (SI′ sites), respectively. However, due to the absence of a peak in the high temperature region (>700 °C), it appears that the NiUSY catalyst does not contain Ni^{2+} ions in its hexagonal prisms [39].

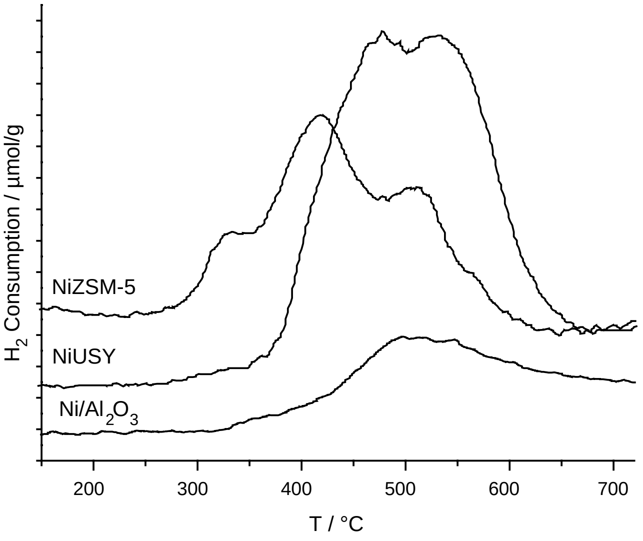

Fig. 5. TPR profiles of Ni-based catalysts.

The NiZSM-5 catalyst shows a TPR profile composed of three peaks, with maxima centered around 326, 416 and 510 °C. The peak near 326 °C can be attributed to NiO-like species which are small enough to escape X-ray diffraction detection and were formed at the outer surface of the sample [40]. The TPR peak with maximum at about 416 °C can be assigned to isolated nickel ions in the charge compensation sites of ZSM-5. The third peak, near 510 °C, is associated to the nickel oxide particles located inside the zeolite channels, which are more difficult to reduce [40,41].

The quantitative TPR analysis of the Ni catalyst profiles gives Ni reduction extent values of 68, 48 and 21.8%, respectively, for NiZSM-5, NiUSY and Ni/γ-Al_2O_3. Thus this study suggests the following sequence of reducibility: NiZSM-5 > NiUSY > Ni/γ-Al_2O_3. Hence, the catalyst which is the most reducible is the most acidic, as shown by NH_3 adsorption microcalorimetry.

3.4. Reactivity

The activity and stability of the catalysts was studied in the reaction of methane reforming by CO_2 performed at 650 °C with a 1:1 CO_2/CH_4 feed ratio. The variations of CH_4 and CO_2 conversions versus time on stream are presented in Figs. 6 and 7, respectively. The performances of the catalysts after 6 h of reaction indicate that no or little deactivation took place within this period. The performance levels of the catalysts stabilize after 1 h, and remain constant beyond 6 h of reaction time. At 650 °C, the NiUSY, NiZSM-5 and Ni/γ-Al_2O_3 catalysts reach, respectively, 71.2, 54.3 and 68.5% of methane conversion, and 71.2, 56.3 and 76.1% of CO_2 conversion, respectively.

According to the stoichiometry of the overall reaction scheme, the carbon dioxide conversion is similar or, in many cases, higher than that of methane, because the reverse water gas shift reaction occurs simultaneously to CO_2 reforming [42,43]: $CO_2 + H_2 \Leftrightarrow CO + H_2O$. This reaction consumes more CO_2 and H_2, and produces more CO.

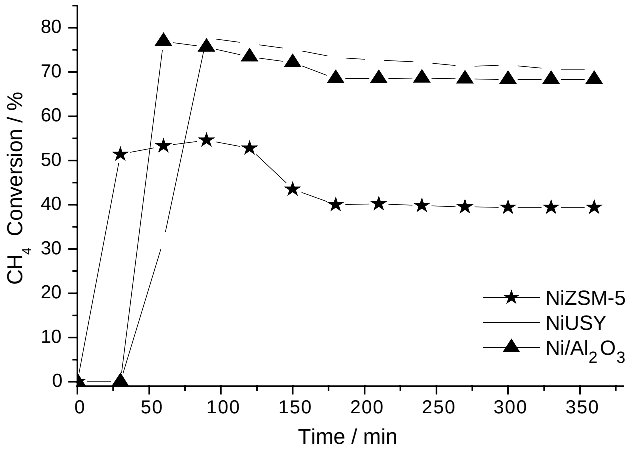

Fig. 6. Evolution of CH_4 conversion vs. time on stream (min) for Ni-based catalysts (P = 1 atm, T = 650 °C, CO_2/CH_4 = 1, D = 1.2 L/h).

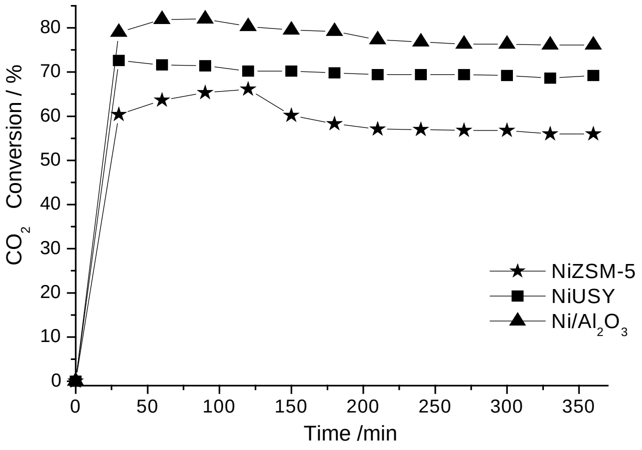

Fig. 7. Evolution of CO_2 conversion vs. time on stream (min) for Ni-based catalysts (P = 1 atm, T = 650 °C, CO_2/CH_4 = 1, D = 1.2 L/h).

As shown in Fig. 8, the carbon monoxide production rates (and hence the syngas yields) are equal to 17.5×10^{-2}, 16.3×10^{-2} and 14.2×10^{-2} mol/g h, respectively, on the Ni/γ-Al_2O_3, NiUSY and NiZSM-5 catalysts. Hence it appears that the catalytic performances of NiUSY and Ni/γ-Al_2O_3 are superior to those of NiZSM-5. The better reducibility of NiZSM-5 compared to NiUSY does not result in improved performance, as observed by Swan et al. [44]. Some authors even consider that excellent catalytic results can be obtained with catalysts containing low amounts of Lewis acid sites [45,46], which is the case of Ni/γ-Al_2O_3 and NiUSY, as shown by CO adsorption calorimetry.

In conclusion, it appears that the catalytic performance of zeolite-based catalysts depends essentially on the structure and physico-chemical properties considered as a whole [37], and of course on the operating conditions of the reaction of dry reforming.

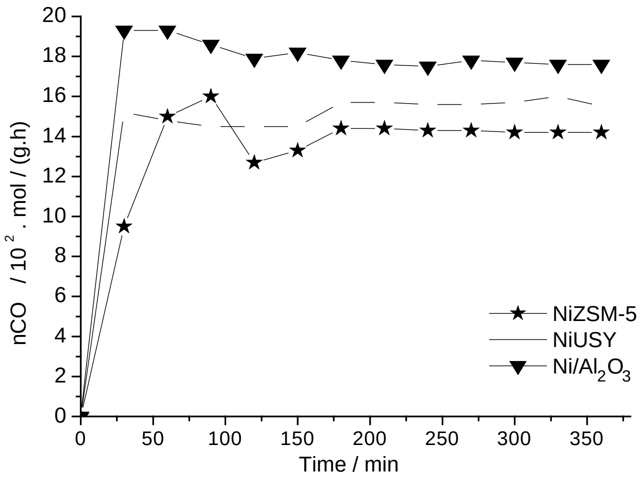

Fig. 8. Evolution of nCO vs. time on stream (min) for Ni-based catalysts (P = 1 atm, T = 650 °C, CO_2/CH_4 = 1, D = 1.2 L/h).

4. Conclusion

In this study, we have investigated catalysts based on HZSM-5 (Si/Al = 14) and USY (Si/Al = 3.5) zeolites exchanged by a solution of nickel nitrate.

The XRD technique has shown that the crystalline structures of the parent zeolites are not affected by the introduction of nickel. Ammonia adsorption microcalorimetry reveals that the most acidic sample is NiZSM-5.

The differential heats of adsorption of carbon monoxide on the NiZSM-5 and NiUSY samples were about 127 and 75 kJ/mol, respectively, at low coverage, and much lower for Ni/γ-Al_2O_3.

Temperature-programmed reduction of these catalysts has shown that reducibility depends on the type of interaction between nickel and the zeolite and the initial position of nickel in the zeolite. This study shows that reducibility varies according to the following sequence: NiZSM-5 > NiUSY > Ni/γ-Al_2O_3.

Our catalysts have also been tested in the reaction of methane reforming by carbon dioxide under atmospheric pressure. The catalytic properties of the NiUSY and Ni/γ-Al_2O_3 catalysts have been found to be superior to those of NiZSM-5.

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