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Deactivation and regeneration of hybrid catalysts in the single-step synthesis of dimethyl ether from syngas and CO_2

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Abstract

Synthesis of dimethyl ether (DME) has been studied in a single reaction step, from H_2 + CO and H_2 + CO_2, in a fixed bed reactor on CuO-ZnO-Al_2O_3/γ-Al_2O_3 and CuO-ZnO-Al_2O_3/NaHZSM-5 hybrid catalysts. It has been proven that water content in the reaction medium (which is higher when CO_2 is fed) contributes to efficiently decreasing deactivation by coke in both catalysts and, consequently, when water is in the feed deactivation is insignificant for 30 h reaction. Nevertheless, water also decreases the activity of γ-Al_2O_3 acid function, due to its high adsorption capacity on the acid sites. Due to its importance in the viability of the industrial process, a study has been carried on the regeneration of both catalysts by coke combustion under controlled conditions (in order to avoid CuO sintering). For this study, the catalysts have been used under severe deactivation conditions. It has been proven that γ-Al_2O_3 does not have a suitable hydrothermal stability and that CuO-ZnO-Al_2O_3/NaHZSM-5 catalyst has an excellent performance and is suitable for using it in uninterrupted reaction–regeneration cycles.

Keywords: Dimethyl ether; Syngas; CO_2; Hybrid catalyst

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1. Introduction

The increasing demand of dimethyl ether (DME) explains the renewed interest in studying processes for its synthesis, which have as reference the STD process originally proposed by Haldor–Topsoe for obtaining DME from syngas on bifunctional catalysts [1,2]. Nowadays, DME is considered as a clean fuel for the 21st century, because it can be applied in automotion, for power generation, in fuel cells and replacing LPG as domestic gas, with low pollutant emission [3–6]. Furthermore, it may replace methanol as intermediate (via syngas) for obtaining light olefins and fuels from alternative sources to oil (coal, natural gas, biomass) [7–12].

The aim of using CO_2 as reactant together with syngas is to contribute to attenuating greenhouse effect. Four reactions take place in the syngas/CO_2-to-DME process:

Methanol synthesis reaction from CO

$$CO + 2H_2 \Leftrightarrow CH_3OH \tag{1}$$

Methanol synthesis reaction from CO_2

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \tag{2}$$

Methanol dehydration reaction

$$2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O \tag{3}$$

Water shift reaction

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{4}$$

There are two strategies for the transformation of H_2, CO and CO_2 to DME: (a) in two reaction steps, firstly, synthesis of methanol on a metallic catalyst and, subsequently, dehydration of methanol to DME on an acidic catalyst and (b) in one step, over a hybrid catalyst provided with the two functions. The process in one reaction step improves the

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yield of DME over the two-step process and increases the viability of CO_2 incorporation, given that thermodynamic restriction is reduced [13–18]. The papers on the synthesis of DME in a single reaction step have approached the study on the effect of the composition of metallic and acid functions of the catalyst and of reaction conditions on DME production and selectivity [19–22]. In these studies, different problems associated with catalyst deactivation are approached.

The aim of this paper is to study minimization of deactivation by coke using the strategy of co-feeding water. This strategy is efficient in the methanol to olefins (MTO) process [23,24]. Nevertheless, it has also been proven that this water adsorption gives way to a significant inhibition in catalyst activity [25]. It is noteworthy that water concentration in the synthesis of DME in a single step is more important when CO_2 is in the feed with syngas, which is due to the water shift reaction, Eq. (4).

Given that industrial viability of the catalyst requires its regeneration, both the metallic function and the acid one must have sufficient hydrothermal stability for recovering its capacity when the catalyst has undergone successive reaction cycles with regeneration by coke combustion between them. Sintering above 300 °C is a potential limitation of CuO as metallic function [26]. Consequently, the coke combustion must be carried out under conditions in which 300 °C are not reached, in order to avoid CuO sintering.

Bearing the afore-mentioned aspects in mind, this paper approaches deactivation and regeneration of CuO-ZnO-Al_2O_3/γ-Al_2O_3 and CuO-ZnO-Al_2O_3/NaHZSM-5 hybrid catalysts, with the aim of establishing the strategies for improving their performance in the synthesis of DME in a single step and under conditions in which CO_2 is fed in a significant amount.

2. Experimental

The catalysts are composed of a metallic function for the synthesis of methanol (CuO-ZnO-Al_2O_3) and an acid function for methanol dehydration to DME (γ-Al_2O_3 and NaHZSM-5 zeolite). These acid functions have low acid strength, in order to minimize the production of light olefins and high molecular weight hydrocarbons, which undergo degradation to coke. The bifunctional catalysts have been prepared by mixing the dry metallic function and the acidic function in aqueous solution at a ratio of 2/1 by mass. This method allows for achieving the best contact between the metallic and acid functions, which gives way to the best performance in conversion, selectivity to DME and yield of DME [19]. The runs have been carried out at 275 °C, under 40 bar, feeding mixtures of (H_2 + CO) and (H_2 + CO_2) at a molar ratio of 4/1 and mixtures of (H_2 + CO) with water at different concentrations. The space time is 8.33 g catalyst h/(mol reactants).

The reaction equipment used, Autoclave Engineers BTRS Jr., is provided with a fixed bed and allows for working up to 100 bar and up to 650 °C. The flow rates of H_2, CO and CO_2 are controlled by Brooks 5850 mass flow meters. The on-line analysis of reaction products has been carried out with an Agilent 6890 gas chromatograph, provided with a flame ionization detector (FID).

The regeneration of the catalyst has been carried out in situ in the reactor at 260 °C with a mixture of air and helium (initially 5% of air) by progressively decreasing the content of helium (only air is introduced at the end). Subsequently, an air stream of 50 $cm^3\ min^{-1}$ is passed for 12 h (for total elimination of coke) and the mixture of air and He is again fed but in this case the air content is progressively decreased. Subsequent to the regeneration, the catalyst is hydrogenated in order to use it in the reaction.

Coke content has been measured by monitoring the gases produced during the combustion by means of EM Thermostar mass spectrometer (Balzers Instruments) coupled to SDT 2960 thermobalance (T.A. Instruments). The area under the CO_2 curve allows for calculating carbon amount in the coke, which practically corresponds to the total amount of coke.

3. Results and discussion

The conversion of CO (X_{CO}) has been calculated by using the flowrates of CO in the feed, $(n_{CO})_0$ and in the reactor outlet stream, n_{CO}

$$X_{CO} = \frac{(n_{CO})_0 - n_{CO}}{(n_{CO})_0} \times 100 \qquad (5)$$

The selectivity to DME (S_{DME}) is determined as the ratio (expressed in %) between the content of carbon in the product DME and the sum of carbon contents corresponding to all the products formed that are present in the reactor outlet stream

$$S_{DME} = \frac{2n_{DME}}{\sum_i n_{C_i} n_i + 2n_{DME} + n_M + (n_{CO})_F + (n_{CO_2})_F} \times 100 \qquad (6)$$

where n_{DME} and n_M are the molar flowrates of DME and methanol in the outlet stream, n_{C_i} the number of carbon atoms for each of the hydrocarbons and n_i is the molar flowrate of these hydrocarbons. The terms $(n_{CO})_F$ and $(n_{CO_2})_F$ correspond to the molar flowrates of CO and CO_2, respectively, formed in the reaction and they are calculated by the difference between the flowrates measured at the reactor outlet, n_{CO} and n_{CO_2} and the values corresponding to the feed, $(n_{CO})_0$ and $(n_{CO_2})_0$

$$(n_{CO})_F = n_{CO} - (n_{CO})_0 \qquad (7)$$

$$(n_{CO_2})_F = n_{CO_2} - (n_{CO_2})_0 \qquad (8)$$

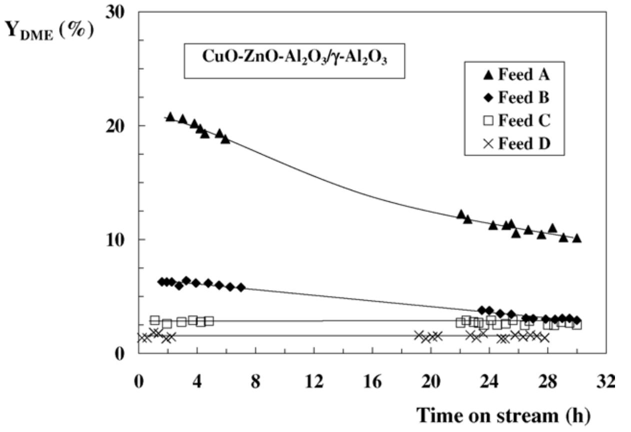

Fig. 1. Evolution with time on stream of DME yield for CuO-ZnO-Al_2O_3/γ-Al_2O_3 catalyst. Feed A = H_2/CO (4/1); feed B = H_2/CO_2 (4/1); feed C = H_2/CO (4/1) with 0.002 ml min^{-1} of water and feed D = H_2/CO (4/1) with 0.004 ml min^{-1} of water.

The terms $(n_{\mathrm{CO}})_F$ and $(n_{\mathrm{CO_2}})_F$ are only considered in Eq. (6) when they have positive values. The yield of DME (Y_{DME}) is measured as the percentage of carbon atoms fed in CO and CO_2 that converts to DME

$$Y_{\mathrm{DME}} = \frac{2n_{\mathrm{DME}}}{(n_{\mathrm{CO}} + n_{\mathrm{CO_2}})_0} \times 100 \tag{9}$$

where $(n_{\mathrm{CO}} + n_{\mathrm{CO_2}})_0$ is the sum of molar flowrates of CO and CO_2 in the feed.

3.1. Effect of water in the deactivation

Figs. 1 and 2 show the effect of feed composition on the evolution with time on stream of DME yield (Fig. 1) and selectivity (Fig. 2), for CuO-ZnO-Al_2O_3/γ-Al_2O_3 catalyst. It is observed that for feed A (H_2 + CO, without water), the values of DME yield and selectivity at zero time on stream are 20.8 and 45.1% (the thermodynamic values are 66.3 and 92.0%, respectively). The yield decreases to 10.1% and the selectivity to 15.0%, subsequent to 30 h time on stream. These decreases with time on stream are mainly attributed to catalyst deactivation by coke. The decrease in selectivity is evidence that coke deposition affects, to a greater extent, to the acid function, which is involved in the transformation of methanol into DME.

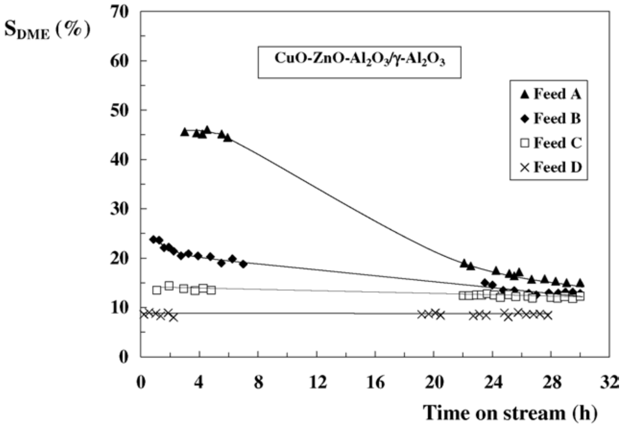

Fig. 2. Evolution with time on stream of DME selectivity for CuO-ZnO-Al_2O_3/γ-Al_2O_3 catalyst. Feed A = H_2/CO; feed B = H_2/CO_2; feed C = H_2/CO with 0.002 ml min^{-1} of water and feed D = H_2/CO with 0.004 ml min^{-1} of water.

When $H_2 + CO_2$ (feed B) is fed, the values of DME yield and selectivity at zero time on stream are significantly lower (the thermodynamic values are: yield 18.6% and selectivity 76.8%). Nevertheless, the decrease with time on stream in the activity of these functions is less pronounced than for the feed of H_2 + CO, which is a consequence of the lower concentration of hydrocarbons formed from methanol and mainly from DME (C_1–C_4 paraffin formation is determined) and of the subsequent lower generation of coke by degradation of these hydrocarbons. The higher concentration of water in the reaction medium due to the water shift reaction (Eq. (4)) contributes to this lower generation of coke. The decrease in the initial yield of DME is partially attributed to the fact that the activity of γ-Al_2O_3 is limited by water adsorption [27]. The lower dehydration capacity of methanol at time on stream zero explains the lower selectivity to DME for the feed made up of $H_2 + CO_2$ compared to the feed made up of H_2 + CO.

The important effect of reaction medium water content in the attenuation of deactivation by coke is evident when the results in Figs. 1 and 2 corresponding to feed A (H_2 + CO, without water) and to feeds C and D are compared. The latter feeds are made up of H_2 + CO with different flowrates of water (0.002 ml min^{-1} in feed C, corresponding to a molar ratio of H_2/CO/H_2O = 4/1/1 and 0.004 ml min^{-1} in feed D). It is observed that, as water content in the feed is increased, the values of DME yield and selectivity at zero time on stream decrease, which is a consequence of water adsorption capacity of γ-Al_2O_3. The effect of water is not the thermodynamic displacement in Eqs. (1)–(4), because although this effect is important the initial yield is lower than the thermodynamic one (21.8% for feed C and 3.4% for feed D). Likewise, the initial selectivity to DME is lower than the thermodynamic one (77.0% for feed C and 46.0% for feed D).

Nevertheless, for feeds C and D both DME yield and selectivity are maintained constant subsequent to 30 h reaction. This efficient limitation of deactivation as a consequence of co-feeding water is explained by water competence with coke precursors in the adsorption on acid sites. This situation has been widely proven in the processes of transformation of methanol into hydrocarbons on different acid catalysts [23–25]. The afore-mentioned results are evidence that co-feeding water is advisable for minimizing deactivation by coke, but that the initial activity of γ-Al_2O_3 is severely affected.

The results in Figs. 3 and 4 are those of DME yield (Fig. 3) and DME selectivity (Fig. 4) obtained in runs carried out under similar conditions but corresponding to CuO-

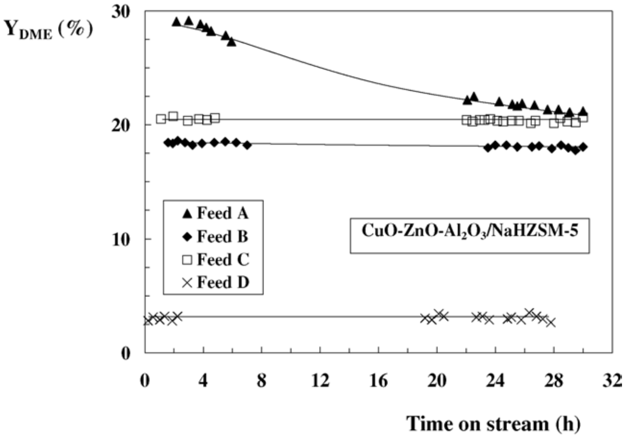

Fig. 3. Evolution with time on stream of DME yield for CuO-ZnO-Al_2O_3/NaHZSM-5 catalyst. Feed A = H_2/CO (4/1); feed B = H_2/CO_2 (4/1); feed C = H_2/CO (4/1) with 0.001 ml min^{-1} of water and feed D = H_2/CO (4/1) with 0.002 ml min^{-1} of water.

ZnO-Al_2O_3/NaHZSM-5 catalyst. It is observed that either feeding H_2 + CO (feed A) or $H_2 + CO_2$ (feed B), when time on stream is increased DME yield and selectivity decrease.

When the effect of water content in the reaction medium is analysed, it is noteworthy that, although DME yield and selectivity at zero time on stream are lower for feed B ($H_2 + CO_2$) than for feed A (H_2 + CO), the difference is lower than the afore-mentioned for CuO-ZnO-Al_2O_3/γ-Al_2O_3 catalyst, which must be attributed to the lower water adsorption capacity of NaHZSM-5 zeolite than γ-Al_2O_3. This behaviour of NaHZSM-5 zeolite has also been observed by Vishwanathan et al. [21]. The difference in the results at zero time on stream for feeds A and B is mainly a consequence of the thermodynamic effect of the change in feed. The lower water adsorption capacity of NaHZSM-5 zeolite gives way to a higher efficiency in the strategy of co-feeding water. Figs. 3 and 4 show that a water flowrate of 0.001 ml min^{-1} (feed C, corresponding to a molar ratio of $H_2/CO/H_2O$ = 4/1/0.5) is enough to avoid deactivation by coke for 30 h without significant limitation of activity due to water adsorption on the zeolite. A greater flowrate of water (feed D) only has an unfavourable effect on the thermodynamics of the overall reaction (Eqs. (1)–(4)).

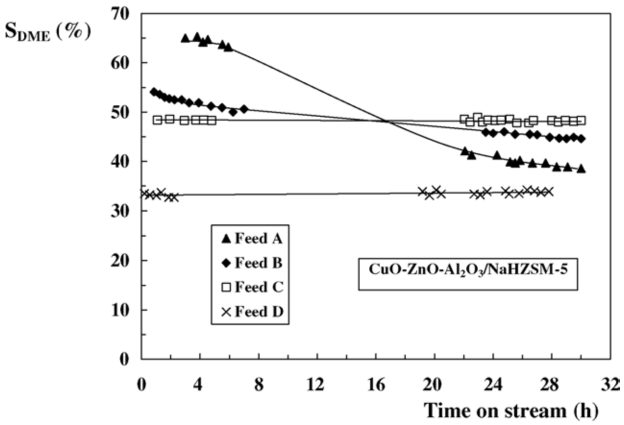

Fig. 4. Evolution with time on stream of DME selectivity for CuO-ZnO-Al_2O_3/NaHZSM-5 catalyst. Feed A = H_2/CO; feed B = H_2/CO_2; feed C = H_2/CO with 0.001 ml min^{-1} of water and feed D = H_2/CO with 0.002 ml min^{-1} of water.

Table 1
Effect of the feed on coke content in the catalysts (wt.%) for 30 h time on stream

Feed	CuO-ZnO-Al_2O_3/γ-Al_2O_3	CuO-ZnO-Al_2O_3/NaHZSM-5
A	3.4	1.6
B	0.8	0.6
C	0.02	0.01
D	0.01	Insignificant

The results shown in Table 1 are evidence of the effect of the feed on coke content in both catalysts. It is noteworthy that for the runs carried out co-feeding water, coke content is insignificant. The coke content in the catalyst is lower for the one based on NaHZSM-5 zeolite, as has already been determined in the literature [18,21] and is explained, on the one hand, by the shape selectivity of the HZSM-5 zeolite and, on the other, by the role of Na as an agent that lowers the acid strength of the sites. Both factors reduce the capacity for formation of hydrocarbons and their condensation to form coke.

3.2. Coke combustion and catalyst regeneration

With the aim of studying coke structure, runs where there is severe deactivation have been carried under the following conditions: feed, $H_2 + CO + CO_2$ (molar ratio: 3/1.5/1); 275 °C; 40 bar; 8.33 g catalyst h/(mol reactants); time on stream, 75 h. Coke combustion in thermobalance subsequent to catalyst stripping with N_2 gives CO_2 and H_2O in the flue gases. Fig. 5 shows a characteristic TPO curve for CuO-ZnO-Al_2O_3/γ-Al_2O_3 catalyst, which is similar to that obtained for CuO-ZnO-Al_2O_3/NaHZSM-5 catalyst. A ramp of 10 °C min^{-1} from 150 to 600 °C has been used. The results are those typically obtained for coke combustion in

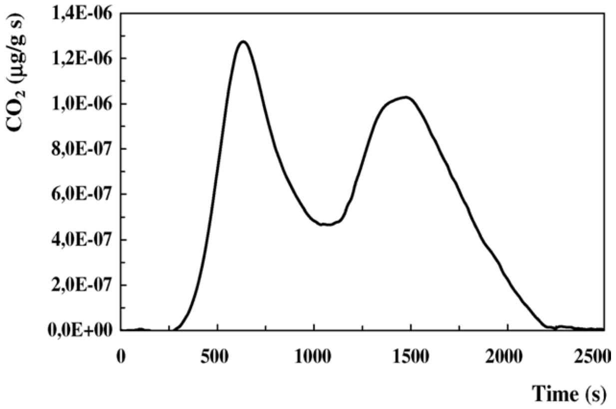

Fig. 5. Results of TPO of the coke in CuO-ZnO-Al_2O_3/γ-Al_2O_3 catalyst.

bifunctional catalysts. The first peak (at 260 °C) corresponds to the combustion of the coke associated with metallic sites, whose combustion (activated by the metallic phase of the catalyst) has a lower activation energy (between 6 and 8 kcal mol^{-1}) than that corresponding to the combustion of the coke associated with the second peak (at 400 °C), whose combustion activation energy is 14–16 kcal mol^{-1}. This more hydrogenated coke is preferably deposited on the acid sites of the catalyst.

Regenerability of the catalysts has been studied by using them in 10 successive cycles of reaction–regeneration. Regenerability is a problem of the acid functions, which has scarcely been studied in the literature [28] and conditions the industrial use of the catalyst. The reaction step has been carried out under the conditions used for the deactivation study, with feed C, for which deactivation by coke is negligible. Subsequent to each reaction step, the catalyst bed is subjected to a 50 cm^3 min^{-1} He stream at 260 °C, prior to coke combustion. This combustion temperature, 260 °C, has been established in order to avoid sintering of CuO, which is known to take place above 300 °C. Coke combustion has been carried with a mixture of air + He in which He content is progressively decreased, in order to avoid hot spots in the catalyst bed.

It has been observed that, as a consequence of the low thermal stability of γ-Al_2O_3, CuO-ZnO-Al_2O_3/γ-Al_2O_3 catalyst does not recover its activity subsequent to regeneration and, consequently, DME selectivity and yield decreases in the successive reaction–regeneration cycles. As the number of cycles is increased, performance reaches an equilibrium state in which DME selectivity and yield are approximately half those corresponding to the fresh catalyst. This behaviour must be attributed to the progressive loss of γ-Al_2O_3 acidity subsequent to successive regenerations.

CuO-ZnO-Al_2O_3/NaHZSM-5 catalyst totally recovers its kinetic performance subsequent to 10 reaction–regeneration cycles, when 30 h reaction steps have been carried out. This result is obtained for all the reactions studied in the reaction step.

4. Conclusions

The results concerning deactivation and regeneration of the catalysts studied are relevant for establishing the reaction conditions (especially those that conditioned water content in the reaction medium) and the acid function for the process of DME synthesis in a single step. The role of water content is esential when CO_2 is fed with syngas.

The deactivation by coke of the catalysts studied may be minimized by co-feeding water with the syngas, given that it competes with coke precursors in the adsorption on acid sites. In fact, when $H_2 + CO_2$ is fed instead of syngas, it performs better from the point of view of limitation of catalyst deactivation by coke, which is due to the generation of water by water shift reaction. Nevertheless, water in the feed has an unfavourable thermodynamic effect and, consequently, the minimum concentration for deactivation by coke to be insignificant must be established.

The coke studied by runs of severe deactivation has two fractions, a hydrogenated one associated with the sites of the metallic function of the catalyst and an evolved one deposited on the sites of the acid function. Consequently, regeneration by coke combustion occurs in two differentiated steps, with different activation energies.

When industrial viability of the catalysts studied is analysed, it has been proven that, although coke deposition attenuates by co-feeding water, the activity of CuO-ZnO-Al_2O_3/γ-Al_2O_3 catalyst at 275 °C is limited due to the fact that water is competing with methanol in the adsorption on γ-Al_2O_3. Furthermore, γ-Al_2O_3 has not enough hydrothermal stability for being used in reaction–regeneration cycles, in which it progressively losses its activity.

CuO-ZnO-Al_2O_3/NaHZSM-5 catalyst performance is suitable for its industrial use in the synthesis of DME from syngas, from $H_2 + CO_2$ mixture or from $H_2 + CO + CO_2$ mixture. For this catalyst, deactivation by coke is insignificant when water is in the feed and, as there is no irreversible deactivation, it may be used uninterrupted as long as temperature is controlled, which must be below 300 °C in order to avoid CuO sintering. Consequently, this catalyst is especially suitable, on the one hand, because it is well-balanced concerning activity–selectivity–deactivation–regenerability and, on the other, water content in the reaction medium is a factor to optimize in the reactor design for DME synthesis in a single step on this catalyst.

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References

[1] J. Topp-Jorgensen, US Patent 4,536,485 to Haldor Topsoe A/S, Denmark, 1985.
[2] J.B. Hansen, F.H. Joensen, H.F.A. Topsoe, US Patent 5,189,203 to Haldor Topsoe A/S, Denmark, 1993.
[3] A.M. Rouhi, Chem. Eng. News 73 (1995) 37.
[4] Haldor Topsoe, Volvo, Statoil, DTI, Demonstration of DME Fuelled City Bus, SAE 2000–1–2005.
[5] http://www.aboutdme.org.
[6] M. Jia, W. Li, H. Xu, S. Hou, Q. Ge, Appl. Catal. A: Gen. 233 (2002) 7.
[7] I. Dybkjaer, J.B. Hansen, Stud. Surf. Sci. Catal. 107 (1997) 99.
[8] Y. Hidaka, K. Sato, M. Yamane, Combust. Flame 123 (2000) 1.
[9] J.S. Hwang, J.S. Ha, S.Y. No, Int. J. Autom. Technol. 4 (2003) 119.
[10] K.H. Song, P. Nag, T.A. Litzinger, D.C. Haworth, Combust. Flame 135 (2003) 341.
[11] K. Takeishi, H. Suzuki, Appl. Catal. A: Gen. 260 (2003) 111.

[12] H.W. Wang, L.B. Zhou, J. Aut. Eng. 217 (2003) 819.

[13] W.J. Shen, K.W. Jun, H.S. Choi, K.W. Lee, Korean J. Chem. Eng. 17 (2000) 210.

[14] J. Wu, M. Saito, M. Takeuchi, T. Watanabe, Appl. Catal. A: Gen. 218 (2001) 235.

[15] A.C. Sofianos, M.S. Scurrell, Ind. Eng. Chem. Res. 30 (1991) 2372.

[16] J. Ereña, J.M. Arandes, J. Bilbao, M. Olazar, H.I. de Lasa, J. Chem. Technol. Biotechnol. 72 (1998) 190.

[17] T. Takeguchi, K.I. Yanagisawa, T. Inui, M. Inoue, Appl. Catal. A: Gen. 192 (2000) 201.

[18] J.H. Kim, M.J. Park, S.J. Kim, O.S. Joo, K.D. Jung, Appl. Catal. A: Gen. 264 (2004) 37.

[19] R. Garoña, Ph.D. Thesis, University of the Basque Country, Bilbao, Spain, 2005.

[20] K. Sun, W. Lu, M. Wang, X. Xu, Catal. Commun. 5 (2004) 367.

[21] V. Vishwanathan, V.K.W. Jun, J.W. Kim, H.S. Roh, Appl. Catal. A: Gen. 276 (2004) 251.

[22] F.S. Ramos, A.M. Duarte de Faria, L.E.P. Borges, J.L. Monteiro, M.A. Fraga, E.F. Sousa-Aguiar, L.G. Appel, Catal. Today 101 (2005) 39.

[23] A.G. Gayubo, A.T. Aguayo, A.E. Sánchez del Campo, A.M. Tarrío, J. Bilbao, Ind. Eng. Chem. Res. 39 (2000) 292.

[24] A.G. Gayubo, A.T. Aguayo, A.L. Morán, M. Olazar, J. Bilbao, AIChE J. 48 (2002) 1561.

[25] A.G. Gayubo, A.T. Aguayo, M. Castilla, A.L. Morán, J. Bilbao, Chem. Eng. Commun. 191 (2004) 944.

[26] H.H. Kung, Catal. Today 11 (1992) 443.

[27] N. Ibarra, Ph.D. Thesis, University of the Basque Country, Bilbao, Spain, 2005.

[28] Y. Fu, T. Hong, J. Chen, A. Auroux, J. Shen, Thermochim. Acta, in press.